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# ON THE FLUORESCENCE AND ABSORPTION SPECTRA OF ANTHRACENE AND PHENANTHRENE IN SOLUTIONS.

By S. Sambursky and G. Wolfsohn.

*Received 17th July, 1939.*

The fluorescence and absorption spectra of anthracene and phenanthrene have been investigated in different solvents,[1] but the wave-length maxima measured by various authors differ appreciably. Most authors assume that both absorption and fluorescence spectra are displaced by a given wave-number in each solvent, when compared with the spectrum in the gaseous state. Banerjea and Mishra,[2] on the other hand, claim that the relative positions of the maxima vary with the solvent, and that the frequency differences between the absorption and the emission maxima can be related to the Raman frequencies of the solvent; according to the general opinion, however, the differences between absorption and fluorescence spectrum in solvents arise as follows [3]: the molecules in the vibrational levels of the excited electronic state revert to the zero level of the excited state without radiation; from this level the molecules then return to the various vibrational levels of the lower electronic state, emitting the fluoresence spectrum. From this mechanism it may be predicted that the frequency differences of the fluorescence spectrum will exhibit vibrational frequencies of the ground state. On the other hand, more recent investigations [4] of the spectra of benzene have shown that in the gaseous state the vibrational levels of the excited electronic state are also involved in the production of the fluorescence spectra.

The object of the present investigation was to measure accurately the absorption and fluorescence spectra of anthracene and phenanthrene in different solvents in order to obtain definite information as to the mechanism of absorption and emission processes in solutions.

## Experimental.

Fluorescence was measured by two methods: (1) In the usual arrangement: fluorescence tube and Hg lamp parallel; the observations were made end-on.

(2) A reduced image of a vertical arc Hg lamp was thrown immediately behind the window of the quartz cell containing the solution. Thus only the foremost layer of the solution was allowed to throw fluorescence light on the slit of the spectrograph. A filter containing approximately 15 % $NiCl_2$ solution was inserted between light source and fluorescence cell.

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[1] D. Radulescu and C. Dragulescu, *Bull. Soc. Chim. Rumania*, 1936, **17**, 9; P. K. Seshan, *Proc. Ind. Acad., Sc. A*, 1936, **3**, 148; *Trans. Faraday Soc.*, 1936, **32**, 689; A. A. Shishlovskij, *Compt. Rend. Acad. Sc. URSS.*, 1937, **15**, 29; P. Pringsheim, *Trans. Faraday Soc.*, 1939, **35**, 15. (For earlier data see Shishlovskij, *loc. cit.*)

[2] G. B. Banerjea and B. Mishra, *Z. Physik*, 1937, **106**, 669.

[3] E. J. Bowen, *Trans. Faraday Soc.*, 1939, **35**, 15.

[4] Sponer, Nordheim, Sklar and Teller, *J. Chem. Physics*, 1939, **7**, 207.

By suitable adjustment of the cell no geometrically reflected light could reach the spectrograph. The light intensity in this arrangement is smaller than in the former, *but there is practically no absorption of fluorescence light by the solution and no influence on the position and intensity of the fluorescence maxima extending into the absorption region.* The fluorescence bands of anthracene were photographed with a Hilger spectrograph ($f = 1$ m.); the absorption bands of anthracene and the spectra of phenanthrene were photographed with a single-prism quartz spectrograph ($f = 60$ cm.). A standard tungsten band lamp with a quartz window provided a source of heterochromatic density marks, from which we could calculate the intensities by measuring the density marks and the spectra by a Moll microphotometer. Purified anthracene (Kahlbaum) and phenanthrene (B.D.H.) were used. The latter contained traces of anthracene (as was evident from the absorption spectrum) which were completely removed by purification according to the method of Clar.[5] Pure phenanthrene does not fluoresce in the visible, and the blue fluorescence described in the literature is due to the presence of anthracene. The absorption bands 3750 Å and 3560 Å frequently attributed to phenanthrene [6] are also due to anthracene.

The continuous spectrum of a hydrogen discharge tube was used as light source for the absorption measurements. The current was kept constant and the continuous light was used for taking the density marks. Anthracene was investigated in a concentration of $1 \times 10^{-4}$ to $3 \times 10^{-5}$ mol./l.; phenanthrene in concentrations of $5 \times 10^{-4}$ to $1 \times 10^{-4}$ mol./l. The fluorescence yield of anthracene reaches its maximum at about $2 \times 10^{-4}$ mol./l. In higher concentrations the mutual interaction of fluorescent molecules leads to extinction, and this probably effects also the position of the band maxima.

## Results.

### 1. Anthracene.

The mean intensity curve of the fluorescence spectra of anthracene in benzene, toluene, chlorobenzene, methanol and hexane solutions respectively is given in Fig. 1. The spectra in these solvents are displaced relatively to each other, but the form of all the curves is identical

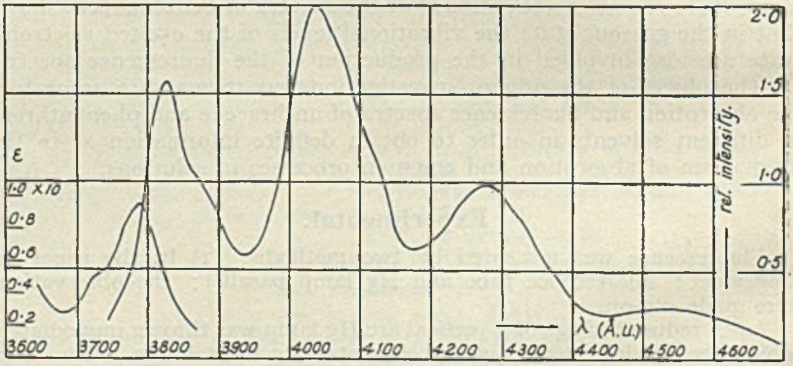

FIG. 1.—Intensity curve of the fluorescence spectrum of anthracene in benzene solution.

(On the left side the first absorption band is drawn in order to illustrate its position relative to the (0′, 0) fluorescence band. The ordinates on the left give the absorption coefficient ε (mol.$^{-1}$ lit. cm.$^{-1}$ × $10^4$).)

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[5] E. Clar, *Ber.*, 1932, 65, 846.

[6] W. V. Mayneord and E. M. F. Roy, *Proc. Roy. Soc.*, 1935, 152, 299; *Landolt-Börnstein. Tab.* 2. *Aufl.*, 1923, 901.

within the limits of the experimental error. It is evident from Fig. 1 that in addition to the constant vibration frequency 1380 cm.$^{-1}$ of the ground state, the vibration bands also show secondary periodicities (frequency 225 cm.$^{-1}$) in the long wavelength side. Approximately the same periodicities are found in the short wavelength side of the absorption bands. The principal frequency difference in absorption corresponding to the excited state (1425 cm.$^{-1}$) is slightly greater than that of the ground state. The fluorescence spectrum of anthracene in solutions can be expressed in the form

$$\nu = \nu_0 - 1380n - 225p,$$

$n$ and $p$ being integers; $\nu_0$ for the different solvents can be found in the first line of Table I.

The most characteristic feature of the fluorescence spectrum of benzene is the frequency 991 cm.$^{-1}$ which corresponds to the totally symmetrical C-vibration of the molecule.[7] The frequency 1380 cm.$^{-1}$ is but slightly smaller than the totally symmetrical Raman vibration 1400 cm.$^{-1}$ of anthracene found by Manzoni Ansidei,[8] and probably identical with the latter, whereas the frefrequency 225 cm.$^{-1}$ does not appear in the Raman spectrum of anthracene. In view of the smallness of this frequency it is doubtful whether it can be regarded as a fundamental one. The secondary maxima due to 225 cm.$^{-1}$ appear in absorption and emission on

TABLE I.—MAXIMA OF THE ANTHRACENE BANDS IN DIFFERENT SOLVENTS.

| Solvent: | | Hexane. | | | Methanol. | | | Toluene. | | | Benzene. | | | Chlorbenzene. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Transition. | Rel. Int. | $\lambda$. | $\nu$. | $\Delta\nu$. | $\lambda$. | $\nu$. | $\Delta\nu$. | $\lambda$. | $\nu$. | $\Delta\nu$. | $\lambda$. | $\nu$. | $\Delta\nu$. | $\lambda$. | $\nu$. | $\Delta\nu$. |
| **(a) Fluorescence.** | | | | | | | | | | | | | | | | |
| (0′, 0) | 1·6 | 3770 | 26,517 | | 3778 | 26,461 | | 3820 | 26,170 | | 3828 | 26,116 | | 3835 | 26,068 | |
| (0′, 1) | 2·0 | 3978 | 25,131 | 1384 | 3987 | 25,074 | 1387 | 4032 | 24,794 | 1376 | 4042 | 24,733 | 1383 | 4050 | 24,684 | 1384 |
| (0′, 2) | 1·0 | 4210 | 23,746 | 1385 | 4220 | 23,690 | 1384 | 4270 | 23,412 | 1382 | 4280 | 23,358 | 1375 | 4290 | 23,303 | 1381 |
| (0′, 3) | 0·3 | 4470 | 22,365 | 1381 | 4480 | 22,315 | 1375 | 4536 | 22,040 | 1372 | 4547 | 21,986 | 1372 | 4561 | 21,919 | 1383 |
| **(b) Absorption.** | | | | | | | | | | | | | | | | |
| (0, 0′) | | 3748 | 26,673 | | 3753 | 26,638 | | 3787 | 26,398 | | 3790 | 26,378 | | 3795 | 26,343 | |
| (0, 1′) | | 3558 | 28,097 | 1424 | 3561 | 28,074 | 1436 | 3593 | 27,824 | 1426 | 3596 | 27,801 | 1423 | 3600 | 27,770 | 1427 |
| (0, 2′) | | 3386 | 29,524 | 1427 | 3388 | 29,507 | 1433 | 3417 | 29,257 | 1433 | 3420 | 29,231 | 1430 | 3424 | 29,197 | 1427 |
| (0, 3′) | | 3230 | 30,950 | 1426 | 3231 | 30,941 | 1434 | 3258 | 30,685 | 1428 | 3261 | 30,657 | 1426 | 3265 | 30,619 | 1422 |

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[7] C. K. Ingold and A. Wilson, *J. Chem. Soc.*, 1936, 941.
[8] R. Manzoni Ansidei, *Rend. Linc.*, 1936, 24, 368.

opposite sides of the main maxima. In contrast to this, in the case of benzene the secondary maxima due to the frequency 160 cm.$^{-1}$ appear on the same side of the main maxima. Therefore we must conclude that the frequency 225 cm.$^{-1}$ in anthracene is not analogous to the frequency 160 cm.$^{-1}$ for benzene, which corresponds in fact to a series of *n*-*n* transitions of a vibration whose frequency in the excited state has dropped by 160 cm.$^{-1}$.

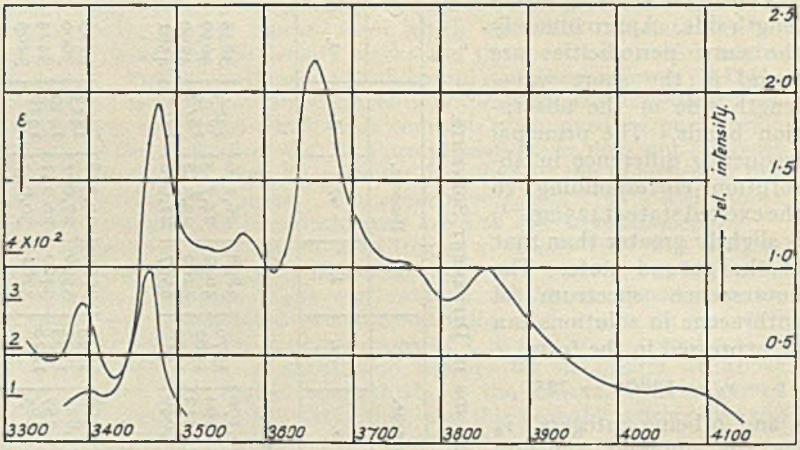

FIG. 2.—Intensity curve of the fluorescence spectrum of phenanthrene. (On the left side the first absorption bands are drawn.)

The figures of Table I show clearly that the hypothesis of Banerjea and Mishra is untenable. Almost the same $\Delta\nu$ appears both in fluorescence and absorption in all solvents. There is no connection between the differences of fluorescence and absorption frequencies and the Raman frequencies of the solvent. In the work of Banerjea and Mishra such a relationship is based on a value for the (0, 0) fluorescence band which is markedly shifted towards the red by absorption (in benzene by 320 cm.$^{-1}$).

## 2. Phenanthrene.

The mean intensity curve of the fluorescence spectra of phenanthrene in benzene and methanol solutions is shown in Fig. 2. As in the case of anthracene, the bands in benzene solution show a shift towards the longer frequencies, when compared with the bands in methanol solutions. Assuming that the excited electronic state consists of two levels and the transitions occur as indicated in Fig. 3, the observed spectra can be easily understood. Absorption measurements made in methanol at temperatures of − 80° C. and + 100° C. showed no influence on the intensity of the two alternating band systems, which proves that the two systems are due to splitting up of the excited electronic level. In Table II the data for phenanthrene are given. As in the case of anthracene there appears in emission a constant vibration frequency which is probably also in this

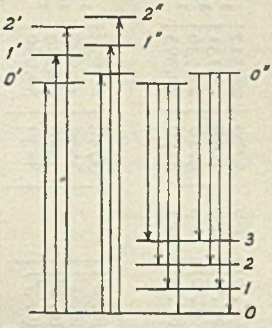

FIG. 3.—Term scheme of the phenanthrene spectra.

case the totally symmetrical Raman frequency. This frequency (1346 cm.$^{-1}$), according to Manzoni Ansidei,[8] is somewhat smaller than the difference 1380 cm.$^{-1}$ found here. A slight asymmetry in the long wave-length side of the stronger bands indicates the existence of a secondary frequency corresponding to the 225 cm.$^{-1}$ frequency of anthracene. As the term scheme in Fig. 3 reveals, the first emission band *o*-*o* (λ 3405 A) is already situated in the region of absorption. The intensity ratio of the two systems is 1·3 : 1 in absorption and about 3 : 1 in emission. The determination of the latter ratio is made difficult by the influence of the stronger bands on the peak intensities of the weaker ones. The fluorescence spectrum of phenanthrene can be expressed in the form

TABLE II.—MAXIMA OF THE PHENANTHRENE BANDS IN DIFFERENT SOLVENTS.

| Solvent : | | Benzene. | | | Methanol. | | |
|---|---|---|---|---|---|---|---|
| Transition. | Rel. Int. | λ. | ν. | Δν. | λ. | ν. | Δν. |
| (*a*) **Fluorescence.** | | | | | | | |
| (*o*′, *o*) | 2·0 | 3480 | 28,727 | | 3463 | 28,868 | |
| (*o*′, *1*) | 2·2 | 3656 | 27,344 | 1383 | 3637 | 27,487 | 1381 |
| (*o*′, *2*) | 0·8 | 3852 | 25,953 | 1391 | 3830 | 26,101 | 1385 |
| (*o*′, *3*) | 0·3 | 4068 | 24,575 | 1378 | | | |
| (*o*″, *o*) | 0·3 | 3405 | 29,360 | | 3556 | 28,113 | |
| (*o*″, *1*) | 0·7 | 3573 | 27,980 | 1380 | 3740 | 26,730 | 1383 |
| (*o*″, *2*) | 0·3 | 3758 | 26,602 | 1378 | | | |
| (*b*) **Absorption.** | | | | | | | |
| (*o*, *o*′) | | 3469 | 28,818 | | 3458 | 28,910 | |
| (*o*, *1*′) | | 3308 | 30,221 | 1403 | 3298 | 30,313 | 1403 |
| (*o*, *2*′) | | 3160 | 31,636 | 1415 | 3151 | 31,727 | 1414 |
| (*o*, *o*″) | | 3392 | 29,473 | | 3381 | 29,568 | |
| (*o*, *1*″) | | 3237 | 30,883 | 1410 | 3228 | 30,970 | 1402 |
| (*o*, *2*″) | | 3095 | 32,301 | 1418 | 3088 | 32,374 | 1404 |

$$\nu = \left.\begin{matrix}\nu_0' \\ \nu_0''\end{matrix}\right\} - 1380\, n,$$

$$\nu_0'' - \nu_0' = 630 \text{ cm.}^{-1}.$$

$\nu_0'$ and $\nu_0''$ for the different solvents are given by the (*o*′, *o*) and (*o*″, *o*) transitions of Table II.

## 3. Effect of Solvents on the Spectra.

Effects of solvents on the spectra of solutes are known and shown clearly by comparison of the spectra obtained in the dissolved state with that in the vapour state. The former are shifted towards the red approximately by equal wave-numbers both in absorption and fluorescence. The same effect is also shown in the present measurements. (See column 1, Table III.) A second effect which seems to be correlated to the shift but has received little attention up to date, is *the frequency difference of the* (*o*, *o*) *band in emission and absorption* (column 2,

Table III). Only in the vapour state is there complete identity in the position of the (*o*, *o*) bands in fluorescence and absorption.* The observed frequencies of the (*o*, *o*) bands in solutions of anthracene and phenanthrene are higher in absorption than in emission. This effect may be explained as follows: Although the non-excited molecules of phenanthrene and anthracene have no dipole moment, it may be supposed *that a dipole moment is formed by excitation.* In general, the direction of this dipole moment will differ from the direction of the internal field of the solvent, and the interaction energy between the field and the dipole will be greater than $kT$. *This interaction energy is transferred to the field before radiation occurs, and therefore the energy difference is smaller in emission than in absorption.* Assuming that the internal field [9] in the solvent is about $10^7$ V./cm., and the dipole moment of the excited molecule of the solute $10^{-18}$ c.g.s. units, an interaction energy of the order of 100 cm.$^{-1}$ results, in good agreement with the figures in Table III. On this assumption spectroscopic estimation of dipole moments of excited molecules is made possible.

TABLE III.—INFLUENCE OF THE SOLVENT ON THE SPECTRA OF ANTHRACENE.

| Solvent. | (1) | | (2) |
|---|---|---|---|
| | $\nu_{\text{hexane}}-\nu_{\text{solvent}}$. Fluor. | Abs. | $\nu_{(o,o')}-\nu_{(o',o)}$. |
| Hexane . . | — | — | 156 |
| Methanol . . | 56 | 22 | 177 |
| Toluene . . | 339 | 270 | 228 |
| Benzene . . | 395 | 331 | 262 |
| Chlorbenzene . | 446 | 331 | 275 |

## Summary.

Photographic-photometrical measurements of the fluorescence and absorption spectra of anthracene and phenanthrene in different solvents lead to the following conclusions:

(1) The vibrational bands of the fluorescence spectra of anthracene and phenanthrene in all solvents have a constant spacing of 1380 cm.$^{-1}$, corresponding closely to the totally symmetrical Raman frequencies of these substances.

(2) Anthracene shows a secondary spacing of 225 cm.$^{-1}$ which cannot be correlated to a known Raman- or infra red-frequency of this molecule.

(3) The excited electronic state of phenanthrene is double, the difference between these levels being 630 cm.$^{-1}$.

(4) The (*o*, *o*) bands in emission and absorption do not coincide, the frequency being larger in the latter. The spacing depends on the nature of the solvent and can be attributed to the energy of interaction between the inner electric field of the solvent and the electric moment of the excited molecules of the solute.

The authors wish to thank Mrs. Th. Wolfsohn for her valuable help in the course of this investigation, and to acknowledge their gratitude to the trustees of the Elizabeth Thompson Science fund for defraying the cost of the comparator used for the wave-length measurements.

*Department of Physics,*
*Hebrew University,*
*Jerusalem, Palestine.*

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* For benzene *cf.* references given in (7).

[9] P. Debye, *Chem. Rev.*, 1936, **19**, 171.

# THE PHOTOCHEMISTRY OF ANTIMONY OXIDE.

By G. Cohn and C. F. Goodeve.

*Received* 31*st October*, 1939.

The sensitivity to light of antimony trioxide when in contact with organic compounds has been observed several times in the laboratory and is well known in the paint trade. Renz[1] found that $Sb_2O_3$ mixed with glycerol turned dark greyish brown when illuminated with sunlight. Later[2] he found a slight photochemical darkening with water alone. When a mixture of $Sb_2O_3$ and saturated $AgNO_3$ solution was shaken in a quartz vessel under Hg-arc lamps, the oxide turned dark grey. There was no oxygen nor metallic silver produced as occurred when CdO, $Nb_2O_3$, or $TiO_2$ were used in place of $Sb_2O_3$. Renz represented the change as

$$5\ Sb_2O_3 \rightarrow 4\ Sb + 3\ Sb_2O_5.$$

He identified antimony metal and $Sb_2O_5$, but his tests for the latter do not appear to be conclusive. He found a small photo-effect with $Sb_2O_4$ but none with $Sb_2O_5$. The fact that paints containing antimony white turn yellowish in ultra-violet light was mentioned by van Hoek.[3]

In this paper are described experiments on the conditions for photochemical changes of $Sb_2O_3$ alone and with other substances.

## The Forms of Antimony Oxide used and their Optical Properties.

Antimony oxide exists in two modifications, an orthorhombic form, valentinite, and a cubic form, senarmontite, the latter being the stable form at room temperature (transition point 573°). Valentinite crystals are built up of chains of molecules and have free valencies on their ends, while senarmontite crystals are built of closed $Sb_4O_6$ units arranged in a face-centred lattice. Valentinite is the more chemically active form and Cagliotti and Milazzo[4] have offered an explanation on crystallographic grounds. The preparation of both senarmontite and valentinite by precipitation is described by Serra,[5] by Bloom and Buerger[6] and by Bloom.[7] It is, however, at present impossible from the method of preparation to be certain of the structure of the substance obtained, and, therefore, all specimens used here have been controlled by taking Debye-Scherrer patterns.

It has long been known that antimony oxide absorbs in the ultra-violet[3] and the reflection curve of one sample has been measured.[8]

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[1] C. Renz, *Helv. chim. Acta*, 1921, 4, 961. [2] *Ibid.*, 1932, 15, 1077.

[3] C. P. van Hoek, *Farben Zeitung*, 1932, 37, 1222, and 1255.

[4] V. Cagliotti and G. Milazzo, *Ric. sci. Progr. tech. Econ. naz.*, 1938, 9, II, 358; *Zentralblatt*, 1939, 1, 3698.

[5] A. Serra, *Z. Kristallogr.*, 1935, 91, 371.

[6] M. C. Bloom and M. J. Buerger, *ibid.*, 1937, 96, 365.

[7] M. C. Bloom, *Am. Mineralogist*, 1939, 24, 281.

[8] C. F. Goodeve and J. A. Kitchener, *Trans. Faraday Soc.*, 1938, 34, 902.

Billy and Berton [9, 10] made semi-quantitative studies of the two forms but give no details of their materials. The absorption spectrum of all samples used here has been determined by the diffuse reflection method.[11] Comparisons were made with MgO which reflects 97 % [12] at all wave-lengths used, *i.e.*, from 550 mμ to 230 mμ.

**Valentinite—samples $Sb_2O_3$ (pr.), and $Sb_2O_3$ (H. and W.).**

A sample, $Sb_2O_3$ (pr.), was prepared by adding crushed crystals of pure $SbCl_3$ to boiling aqueous ammonia, washing until free from $Cl^-$ and drying in a desiccator (first over $CaCl_2$ under vacuum, then over $P_2O_5$). The powder was a clear white. The Debye-Scherrer pattern was identical with a pattern taken with natural valentinite, which pattern is easily distinguishable from that of senarmontite.[8]

The diffuse reflection of $Sb_2O_3$ (pr.) falls rapidly at about 385 mμ (see curve I in the Fig.) indicating that strong absorption sets in at this wave-length. The diffuse reflection spectrum of powdered natural valentinite is also shown (curve II) and it is seen that it is near to that of $Sb_2O_3$ (pr.).

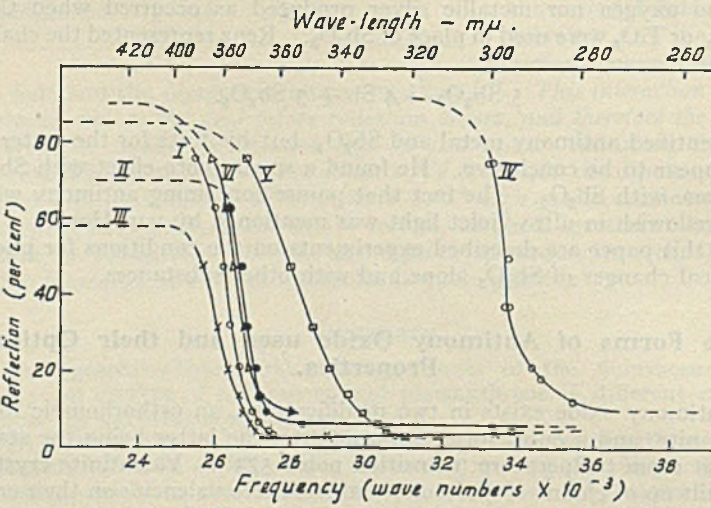

Fig. 1.—The Reflection spectra of different samples of antimony oxide. Curve I—(pr.) and (H. and W.), II—natural valentinite, III—(H. and W.) heated to 400°, IV—Senarmontite (sub.), V—(hyd.) I, VI—(hyd.) III.

The transmission spectrum of a thin flake of natural valentinite 0·02 mm. thick showed a sharp threshold at about 365 mμ, the absorption at this wave-length being about 75 %. Thicker flakes showed absorption at slightly longer wave-lengths, but as they were not clear, no quantitative measurements could be made. The spectrum of the light reflected from the flake was found to have a marked depression in intensity, beginning at 368 mμ with a rise to almost the original value at 360 mμ. This is probably due to the fact that at wave-lengths longer than 368 mμ reflection comes from both surfaces, while absorption below this wave-length reduces the reflection from the back surface. The subsequent rise may be due to an increase in refractive index associated with the increase in absorption and hence increased reflection from the front surface. Billy and Berton [9]

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[9] M. Billy and A. Berton, *Comptes rendus*, 1938, **206**, 1631, 1958.

[10] A. Berton, *ibid.*, 1938, **207**, 625.

[11] See, for example, C. F. Goodeve, *Trans. Faraday Soc.*, 1937, **33**, 340.

[12] J. Preston, *Trans. Opt. Soc.*, London, 1930, **31**, 15; and Taylor, *J. Opt. Soc. Am.*., 1934, **24**, 192.

found a minimum in the diffuse reflection of powdered valentinite at 362 m$\mu$ followed by a rise to a maximum at 355 m$\mu$. They attributed the rise to a decrease in absorption, but it is more likely that it is due to the same cause as above, *i.e.*, increased reflection on front surfaces. Microphotometer curves of our spectrum plates for powdered valentinite did not show such a rise but only a slight inflexion at about 360 m$\mu$.

The sample $Sb_2O_3$ (H. and W.), was commercially pure and supplied by Hopkin and Williams. It was a fine powder with a faint brownish yellow tint which disappeared when the powder was stored in the dark over $P_2O_5$, but not when in contact with the atmosphere. The Debye-Scherrer pattern and the reflection spectrum were identical in every respect with those of $Sb_2O_3$ (pr.), showing that the substance was valentinite.

Both samples contained water (perhaps also traces of excess oxygen). Simon and Poehlmann [13] have shown that there exist no hydrates of $Sb_2O_3$. Water accordingly could be removed by storing over $P_2O_5$, although only very slowly; after eight months' drying there was still water in the samples. The water was given off rapidly when the substances were heated in vacuum, the bulk of the water coming off at about 250°. Two samples of (H. and W.) kept in vacuum for two hours at about 350° and 400° respectively turned a little greyish, but the Debye-Scherrer patterns and the threshold of absorption (see Curve III) were unchanged, showing that, even with this treatment, the valentinite had not changed into the stable modification. (In order to compare Curve III with Curve I the former should be multiplied by 1·45, *i.e.*, the ratio of the reflections in the visible.) Samples of $Sb_2O_3$ (pr.) and of $Sb_2O_3$ (H. and W.) dried over $P_2O_5$ for 2½ months at room temperature gave by titration with $KBrO_3$ 99·4 % and 98·6 % $Sb_2O_3$ respectively, indicating a higher water content of the latter. No change in the reflection spectra could be detected after 8 months' drying.

**Senarmontite—sample $Sb_2O_3$ (sub.).**

Clear colourless crystals of pure senarmontite were prepared by sublimation of $Sb_2O_3$ (H. and W.) at 400° to 500° and at $10^{-2}$ mm. pressure. The crystals which were octahedral, of sizes up to 1 mm., were generally crushed before use. Their Debye-Scherrer pattern was identical with that shown for senarmontite.[6] The threshold of absorption was found at 300 m$\mu$ (see curve IV) in agreement with the observation of Billy and Berton.[9] This means that the principal absorption band of the senarmontite unit, $Sb_4O_6$, begins at about this wave-length. The diffusely reflected light from the unpowdered crystals, however, showed the presence of absorption up to 340 m$\mu$. The average light path in this case traverses a much thicker layer of crystal, and therefore weaker absorption shows up.

**Samples prepared by Hydrolysis, $Sb_2O_3$ (hyd.).**

Bloom[7] found that the products obtained by hydrolysis of antimony salts which had been dissolved in the respective acids depended upon the concentration of the free acid, higher concentrations favouring valentinite. Certain mixed forms were described by Bloom and Buerger.[6]

A sample, $Sb_2O_3$ (hyd.) I, prepared by dissolving $SbCl_3$ in HCl, neutralising the excess with $Na_2CO_3$ and adding drop by drop to a large excess of boiling water, showed only very few and rather diffuse Debye-Scherrer lines that suggested that the substance was senarmontite. Its reflection spectrum is shown by Curve V, and while it does not agree with that of senarmontite the difference could be accounted for if we assume that there is only a trace of valentinite present. It is probably a transition form.

On the other hand, slight alterations in the procedure gave different results. Solution of $SbCl_3$ in HCl, addition of cold water until a precipitate just formed, filtration and addition of the clear filtrate to boiling water

[13] A. Simon and H. Poehlmann, *Z. anorg. Chemie*, 1925, 149, 101.

which was kept boiling for 90 minutes, gave a well-crystalline product (hyd.) II, whose pattern and spectrum were identical with those of valentinite. A sample prepared by addition of $SbCl_3$ crystals directly to cold water and washing by decantation with boiling water gave a product (*e.g.*, sample (hyd.) III) whose pattern, while indicating that it was well crystallised, was quite different from that of either senarmontite or valentinite. Neither the pattern nor the crystal shape was entirely reproducible. The reflection spectrum of (hyd.) III, Curve VI, was almost identical with that of powdered valentinite.

These results do not easily fit in with those of Serra [5] or of Bloom and Buerger [6] although they are nowhere in direct conflict. In agreement with the latter authors we found it impossible to remove all of the chloride from samples prepared by hydrolysis. Considerably more systematic work would be necessary before the conditions could be standardised to produce a given form. The importance of this preliminary work lies in the fact that the photosensitivity of antimony oxide prepared by hydrolysis has been shown to be considerably less than that of other crystalline forms (see Obs. 6 and 20, below). It appears that the reflection spectrum is not sensitive to all changes in crystal form (*cf.* Billy and Berton [9]).

## The Darkening of Antimony Oxide by Light.

Samples of the above preparations were exposed to the full light of the mercury arc (usually a Hanovia low pressure type) in theopen or in flat quartz illuminating vessels at a distance of about 15 cm. Most of the observations have been repeated several times.

The results are summarised as follows :—

(1) $Sb_2O_3$ (H. and W.) showed visible yellowing in 5 seconds, turning to light brown in 30 minutes. There was practically no further change up to several hours.

(2) The efficiency of darkening was independent of light intensity—an exposure four times as long with light four times as weak gave an identical darkening.

(3) The rate was unchanged by addition of liquid water. After five hours' illumination of a stirred mixture, a test for $H_2O_2$ with $Ti(SO_4)_2$ was negative.

(4) $Sb_2O_3$ (pr.) behaved as in (1) except that it was slower.

(5) Valentinite (natural) and senarmontite ($Sb_2O_3$ sub.) were not sensitive to irradiation. The latter showed no visible colouring after 5 hours' exposure. It is therefore at least 2000 times less sensitive than (H. and W.). Addition of water did not induce sensitivity.

(6) All samples of $Sb_2O_3$ (hyd.) were found to be insensitive either in the presence or absence of water.

(7) Drying of $Sb_2O_3$ (H. and W.) over $P_2O_5$ for a few days produced no change in sensitivity, but after 6 months the illumination necessary to produce noticeable darkening was 100 times longer than that for an undried blank. The final degree of darkening was also much less.

(8) Drying $Sb_2O_3$ (H. and W.) by baking for half an hour at 350° in a vacuum rendered it completely insensitive. Addition of water did not restore any sensitivity in 8 hours, but on keeping in the atmosphere for 14 days a slight sensitivity was found.

(9) (H. and W.) which was irradiated under vacuum in the cold darkened at the same rate as in observation (1). On heating the *darkened* sample under vacuum to 250° it quickly faded to its original white. This temperature coincides with that at which there is a rapid loss of water.

(10) A sample (H. and W.) thoroughly darkened as in (9) did not fade appreciably after 12 months in air over $P_2O_5$ in the dark.

(11) Extensive attempts were made with (H. and W.) and (pr.) to test whether oxygen was evolved in the photochemical change. A highly

evacuated quartz vessel, 8 × 1·5 × 0·3 cm., containing the sample, was connected to a capillary discharge tube, the spectrum of which could be examined by means of a Hilger quartz Raman spectrograph, exposure 10 to 60 sec. It was impossible to obtain completely conclusive results owing to the adsorbed water (and possibly oxygen) which was evolved by illumination in the cold (due to heating by the light from the arc, even when filtered from infra-red). The water dissociated in the discharge and gave the oxygen spectrum. If it was removed by heating to 350° the powder became insensitive, but a partially effective compromise was obtained by heating to 100° in vacuum for one hour. Subsequent illumination in the cold gave darkening but no gas evolution. In one experiment illumination for 8 hours gave a darkening which should have produced a pressure of oxygen at least of the order of 10 mm. (assuming the maximum possible extinction coefficient, $10^{-16}$ cm.$^2$, for the dark substance). The accuracy of the tests was sufficient to show that the oxygen pressure could not have been anything like as high as this. It is therefore to be concluded that no appreciable free oxygen is evolved in the photochemical darkening process.

### Wavelength Considerations.

Preliminary experiments with filters confirmed the expectation that the darkening described above occurred with ultra-violet and not with visible or infra-red light. Later, the threshold of photosensitivity was accurately determined simply by exposing a glass plate covered with the powder in the high-aperture Raman spectrograph. The powder $Sb_2O_3$ (H. and W.) was made into a thin paste with water, painted on to the glass plate and dried in the dark in a desiccator. Exposures to a pointolite lamp of various times from 5 to 20 hours showed that a very sharp threshold of darkening occurred at 375 $m\mu$. Its position was unchanged by the presence of glycerol (see obs. 13). The agreement between this threshold and that of absorption (see Fig.) is satisfactory and indicates that the substance giving rise to this absorption is responsible for initiating the photochemical process (glycerol does not absorb except in the far u.v.).

Using a Hg-arc lamp, a series of exposures on $Sb_2O_3$ (H. and W.) were compared with a similar series on an ordinary AgBr photographic plate (at, of course, an enormously reduced range of exposures) and showed that from 365 $m\mu$ to below 240 $m\mu$ the sensitivity of $Sb_2O_3$ was parallel to that of AgBr. As the photosensitivity of the latter is almost independent of wave-length over this range [14] we can conclude that that of $Sb_2O_3$ is also independent of wave-length.

### The Photo-Darkening of Antimony Oxide in the presence of other Reagents.

For the tests summarised below the powder was placed in the cavities of a porcelain test plate and sufficient liquid or solution added just to cover it. The whole was covered by a quartz plate, cooled by an air stream and illuminated with a Hg-arc as before. All results have been repeated at least twice and there were full comparison blanks to test the absence of thermal effects, etc.

(12) The rate of darkening of $Sb_2O_3$ (H. and W.) is uninfluenced by added water, butyl or amyl alcohol, formaldehyde or linseed oil varnish. $Sb_2O_3$ (sub.) remained insensitive in the presence of these reagents.

(13) The rate of darkening of (H. and W.) and (pr.) was increased by the addition of glycerol (commercial or "Analar") and the final degree of darkening was a deep black, much stronger than that obtained with the dry powder (*cf.* obs. 1). This final state was attained in about 40 minutes. There was also an increase with ethylene glycol and sugar solutions.

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[14] Private communication from Dr. E. S. Sheppard, Eastman Kodak Co., Ltd.

(14) $Sb_2O_3$ (sub.) in the presence of glycerol darkened at a *faster* rate than did (H. and W.) in obs. 13. A filter cutting out all light below 330 m$\mu$ stopped the reaction entirely. (Compare absorption of senarmontite.) The presence of 25 % of water in the glycerol had no effect, but with 50 % the reaction practically ceased (*cf.* obs. 16).

(15) Natural valentinite darkened with glycerol.

(16) $Sb_2O_3$ (sub.) which had been darkened as in obs. 14, returned to its original white when left in the room for about a day. The cycle was repeated several times on the one sample. If left in dried air or in pure water vapour at room temperature the reversal was very much retarded. Addition of liquid water or methyl or ethyl alcohol to samples darkened as in obs. 14 caused an almost immediate reversal. Acetone, which is not soluble in glycerol, caused no effect.

(17) $Sb_2O_3$ (H. and W.) or (pr.), darkened as in obs. 13, did not whiten again but returned to that brownish shade which would have been obtained by irradiating the powder alone.

(18) Hydroxylamine hydrochloride, hydrazine hydrate and sulphate and KI solutions all gave higher rates than in obs. 13, and the darkening was *irreversible.* With the nitrogen compounds gas was evolved. There was no thermal reaction even at 100°. $Sb_2O_3$ (sub.) with these substances darkened at a slightly lower rate, presumably due to the fact that it absorbs only the further ultra-violet.

(19) The brown powders of obs. 1 and 3 and the black powders of obs. 13 and 14 were completely soluble in HCl, giving colourless solutions. The black powder of obs. 18, however, left a residue of black particles. Antimony metal, having a normal potential with respect to hydrogen of approximately + 0·2 volts [15] should be insoluble in acids, but may become soluble due to the small size of the particles in obs. 1, 3, 13 and 14, and to the presence of oxygen. The black residue from obs. 18 consists, presumably, of larger particles of antimony metal. The solubilities in HCl are parallel to the observations of the reversibility of the darkening; samples showing reversal being soluble, the others not.

(20) Samples of $Sb_2O_3$ (hyd.) in contact with glycerol darkened at a lower rate and to a lower final extent than any other preparation; (hyd.) III was less sensitive than (hyd.) I or II.

(21) $Sb_2O_3$ (H. and W.) is also able to act as a photosensitiser in a way similar to $TiO_2$.[8] Dyes such as methylene blue, chlorazol orange POS and chlorazol sky blue FF were readily decolorised when adsorbed on $Sb_2O_3$ and exposed to a Hg-arc; whereas comparison samples adsorbed on $BaSO_4$ were unchanged.[16] There was no obvious darkening of the $Sb_2O_3$.

## Conclusions.

In any photosensitive system there must be present a light absorbing species and a potentially-reactive centre. If these are separated, it is necessary to postulate a mechanism by means of which the energy of the quantum may be transferred as a more or less complete unit, an "exciton" from the point of absorption to the centre. Two such mechanisms have recently been discussed.[8, 17] The success of the transference of the energy of the quantum to the potentially reactive centre depends upon the competition with the process of degradation of this energy to heat, or with fluorescence. None of the samples, however, showed fluorescence.

In all observations recorded above (with the exception of obs. 18) it has been shown that the absorption was associated with the antimony

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[15] *Landolt-Borenstein II. Ergbol.*, p. 971.

[16] J. A. Kitchener, *Unpublished Experiments.*

[17] C. F. Goodeve, *Nature*, 1939, 143, 1007.

oxide, but that the threshold of absorption depends upon the arrangement of the atoms. There is no possibility of the absorption being due to irregularities in the crystal lattice as suggested by Gurney[18] for ZnS, as the precipitated powders give the same absorption as the pure crystals.

The conditions for sensitivity to light, which are presumably determined by the potentially-reactive centre, are concerned with both the crystal lattice and the presence of some second species, either water (obs. 7 and 8) or certain reducing agents (obs. 13-20). The mechanisms, however, of the processes with water and with the other substances are apparently different, and are therefore to be considered separately.

The photochemical change with water might be called an *internal* process. The water must be " built in " to the crystal lattice in a special manner (*cf.* obs. 7 and 8 with 3); it cannot enter completed valentinite or senarmontite lattices. It apparently can re-enter slowly a valentinite lattice from which it has been removed (obs. 8). The photochemical process appears to be a reduction of antimony oxide to the metal, the oxygen being retained in a neighbouring position. This would account for the reversal of the darkening and for the absence of evolved oxygen (obs. 11). It is possible that water acts by distorting the lattice, thus facilitating the photodecomposition and then stabilises the new chemical arrangement; otherwise the antimony, which is so finely divided that it dissolves in HCl, would be re-oxidised immediately on contact with air (*cf.* obs. 16). That the stabilisation is fairly complete is shown by the fact that the reversal of the process takes place appreciably only on the removal of water by heating (obs. 9). It is of interest to point out that zinc sulphide, which blackens with light in the presence of water, shows a reverse reaction at room temperature.[19] Reactive centres of valentinite with water are independent of those formed with glycerol (obs. 17). The " internal darkening " does not cease because of protection against the radiation by absorption by the products, but rather when all of the potentially reactive centres have been used up (obs. 1 and 7).

The " external " photochemical reduction of $Sb_2O_3$ by reducing agents is of especial interest. Their activity is highly specific and does not depend only on their ordinary reducing power (*cf.* obs. 12 and 13-19). With strong reducing agents, such as $N_2H_4$ or $NH_2OH$, all $Sb_2O_3$ centres, including those with water, are attacked photochemically with the formation of Sb metal. The reduction is irreversible and the metal does not dissolve in HCl. With glycerol the reaction is reversed, presumably when the protective action of the glycerol is destroyed. This apparently occurs when the viscosity is lowered and oxygen can be taken up more rapidly. As the metallic reduction product dissolves in HCl, it is to be concluded that it is in a finely divided state.

All reactive centres containing $Sb_2O_3$ (hyd.) were the least sensitive of any, a fact which may be of practical importance. This low sensitivity might be attributed either to the chloride present or to a strong tendency for degradation of electronic energy to heat in such irregular lattice structures (see Frenkel[20]). The effect is parallel to the inhibiting action of adsorbed sulphate on $TiO_2$.[21]

[18] R. W. Gurney, *Trans. Faraday Soc.*, 1939, 35, 98 and 143.

[19] N. T. Gordon, F. Seitz and F. Quinlan, *J. Chem. Physics*, 1939, 7, 4.

[20] J. Frenkel, *Physik. Z. Sow.*, 1936, 9, 158.

[21] C. F. Goodeve and J. A. Kitchener, *Trans. Faraday Soc.*, 1938, 34, 572.

The authors are indebted to Dr. J. A. Kitchener and Mr. M. R. Taylor for their kind assistance, and to Mr. F. A. Bannister of the British Museum, Department of Minerology, for the provision of samples of valentinite.

## Summary.

The photochemical sensitivity and the absorption spectra of the different crystalline forms or states of $Sb_2O_3$ have been investigated. All forms are sensitive to irradiation only when some foreign substance is present. There are two different types of photoreaction, both apparently with formation of antimony metal. The orthorhombic form of $Sb_2O_3$ is able to " build in " water forming an internal photoactive system. The reaction is reversed by removal of the water. With certain reducing agents an external photodecomposition occurs with all forms of $Sb_2O_3$. Little or no sensitivity was shown by samples prepared by hydrolysing $SbCl_3$ with water. With glycerol the reaction is reversed if oxygen together with water or other liquid miscible with glycerol are taken up.

*The Sir William Ramsay and Ralph Forster*
*Laboratories of Chemistry,*
*University College, London;*
*and Kemiska Institutionen, Tekniska Högskola, Göteborg.*

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# DIELECTRIC LOSS IN POLYSTYRENE MIXTURES.

By F. C. Frank and Willis Jackson.

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During recent years a number of investigators have sought to clarify the mechanisms underlying the energy loss which occurs in dielectrics when they are subjected to alternating electric fields. In this connection the authors have previously studied the behaviour of paraffin waxes containing small percentages of known polar " impurities " and endeavoured to correlate the experimental results obtained with the dipole theory of Debye.[1, 2]

This theory predicts that the dielectric loss due to a polar constituent present in a non-polar dielectric medium will pass through a maximum with variation either of the temperature or of the frequency of the applied electric field, and relates the height of this maximum to the dipole moment and concentration of this polar constituent. The concentration is assumed to be sufficiently small to ensure the absence of interaction between individual polar molecules, and in the paraffin wax solutions referred to, where this condition was satisfied, the quantitative agreement between the observed and calculated loss maximum was good, in spite of the fact that the physical concepts on which the original theory is based seem quite unsuited to the solid state.

The theory also relates the position of the dielectric loss maximum in the spectra of frequency and temperature to the size of the orienting

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[1] W. Jackson, *Proc. Roy. Soc. A.* (1935), **150**, 197.

[2] F. C. Frank, *Trans. Faraday Soc.* (1936), **32**, 1634.

polar group and the viscosity of the environment in which it is situated, and the uncertainty attaching to the applicability of the theory in the above case was emphasised when on calculation it was found that the "apparent viscosity" of the solid paraffin wax medium at room temperature to the orientation within it of polar molecules of similar structure was less than 10 poise.

By way of extending the scope of the measurements into a range of materials considerably harder than paraffin wax, it was decided to investigate the possibility of using polystyrene. This substance, which as a hydrocarbon is practically free from dielectric loss over the whole of the frequency range from 50 to $10^6$ cycles per second, is available commercially as a thermo-plastic moulding material under the name of Trolitul. The practical problem was to prepare plates of this substance, containing small percentages of various substances, whose effect on the dielectric properties could be anticipated from the dipole theory, of a size (6 in. diam. × $\frac{1}{16}$ in. thick) and quality suitable for the dielectric measurements.

## Preparation of the Test Specimens.

At the preliminary stage a number of specimens were prepared from a granulated form of the material in the I.C.I. research laboratories, employing the normal high-pressure moulding technique. Lower temperatures and longer moulding times were used than in the method finally adopted, and some of the samples (*e.g.* those containing small percentages of benzoic acid and *p*-toluidine) caused great difficulty by sticking to the moulds. The added substances also crystallised out from mixtures of a concentration which gave perfectly clear mouldings by the subsequent low-pressure method. The surface of the plates was unsatisfactory and the specimens showed appreciable distortion, which became very marked on heating to the softening temperature.

In the low pressure method developed in the laboratory the major difficulty was that of removing air bubbles without reaching temperatures productive of depolymerisation and oxidation. The various polar materials added to the polystyrene acted to some extent as plasticisers and assisted in this process, but it was sometimes necessary to add a little naphthalene also.

The technique finally adopted was as follows : The mixture was placed in an enamel dish, covered with a clock glass and clamped rigidly in an oil bath, and heated to a temperature at which easy stirring became possible. This temperature was usually between 200 and 250° C., but was kept as low as possible so as to reduce fuming, oxidation and boiling out of the added substance during the mixing process. The mixture was alternately stirred and left to stand at this temperature and then taken up to about 290° C. for a short time to free it from bubbles. It was then cooled to about 260° C., which was found to be a convenient temperature for pouring.

The mixture was poured on to a hot flat plate of brass and pressed into shape with another similar plate fitted with a lifting handle, and with three set-screws at its edge to determine the thickness of the final specimen. A thin film of vaseline rubbed over the plates ensured that they could be lifted away from the specimen on cooling to room temperature, although cooling with ice was occasionally necessary.

Satisfactory mouldings were produced of the following mixtures :—

(*a*) 17·5 % butyl phthalate.
(*b*) 16·3 % chlorinated diphenyl. ("Permitol"—a mixture approximating to tetrachlordiphenyl.)
(*c*) 7·95 % β-naphthol + 3·5 % naphthalene.
(*d*) 12·8 % β-naphthol.
(*e*) 4·8 % cetyl palmitate + 2·3 % naphthalene.

## The Dielectric Loss Measurements.

The measurements consisted of a study of the variation of the dielectric loss factor—tan δ—with temperature at convenient frequencies in the range $10^6$-$10^7$ cycles per second. The method employed was a resonance substitution one, the circuit diagram for which is shown in Fig. 1. In order to avoid any assumption regarding zero loss in the comparison air condenser, and at the same time to allow for any residual loss in the test condenser not arising from the inserted dielectric, use was made of two condensers C and $C_x$ of identical construction. A description of these condensers and of the arrangement for their temperature variation has been given elsewhere.[1] The dielectric to be investigated was placed in $C_x$ and the capacitance of C, having air dielectric, was then adjusted until it equalled that of $C_x$. When this adjustment had been made the circuit remained in resonance to the frequency of measurement when the condenser was changed from $C_x$ to C at the switch S. The loss factor of the dielectric of $C_x$ was derived from the difference between the total circuit loss when the capacitance was formed by $C_x$ and by C. The loss in each case was deduced from the width of the resonance curve delineated on the thermionic voltmeter by suitable incremental changes in the oscillator frequency about the resonant value.

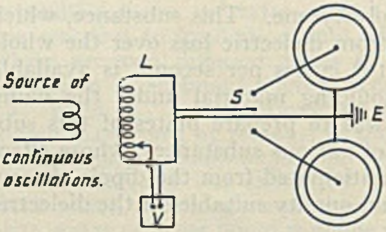

FIG. 1.

$C_x$—test condenser,
C—identical air condenser,
S—change-over switch,
E—earth point,
V—thermionic voltmeter.

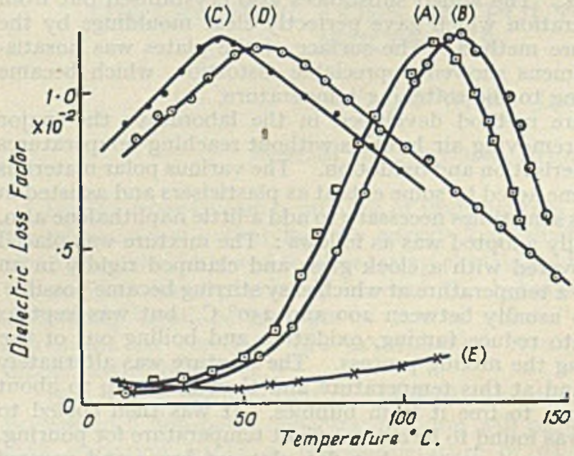

FIG. 2.

*Curves* (A) *and* (B)—Chlorinated diphenyl mixture.

(A)—$10^6$ cycles,
(B)—$4{\cdot}8 \times 10^6$ cycles per sec.

*Curves* (C) *and* (D)—Butyl phthalate mixture.

(C)—$0{\cdot}82 \times 10^6$ cycles,
(D)—$7{\cdot}5 \times 10^6$ cycles per sec.

*Curve* (E)—Cetyl palmitate mixture.

Frequency $5 \times 10^6$ cycles per sec.

The experimental results on the moulding mixtures previously referred to are given in Figs. 2 and 3.

## Discussion.

The results demonstrate that the hard polystyrene environment imposes no very severe restriction on the orientation within it of polar molecules of the type considered. The curves (A) and (B), Fig. 2, relating to the moulding containing *chlorinated diphenyl* are of particular interest in view of the fact that the behaviour of this material in bulk has been studied by one of the authors.[3] At a frequency of $0{\cdot}95 \times 10^6$ cycles, closely that to which curve (A) relates, the chlorinated diphenyl alone gave a very sharp loss maximum at a temperature of 26° C. when the material was a liquid of viscosity coefficient about 100 poise. The polystyrene environment has had the effect of shifting the position of the loss maximum to 110° C., and further of broadening the loss—temperature curve—reckoned at half its height—from 13° C. to 60° C. These curves (A) and (B) are indeed very much broader than the theoretical form, and this is no doubt to be accounted for on the grounds that the complicated structure of the polystyrene glass provides a wide range of different environments for the orienting polar molecules. The absence of appreciable dielectric loss at 26° C. suggests that the chlorinated diphenyl molecules are not clustered to any very considerable extent.

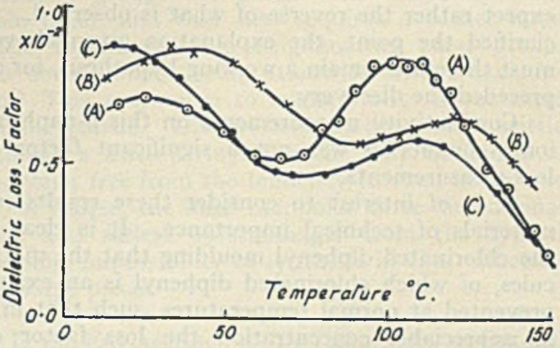

FIG. 3.

β-naphthol mixture.

(A)—$0{\cdot}8 \times 10^6$,
(B)—$5{\cdot}25 \times 10^6$,
(C)—$0{\cdot}66 \times 10^6$
cycles per sec.

(Measured in order A, B, C; with rising temperature in each case.)

The *butyl phthalate* curves (C) and (D), Fig. 2, are extraordinarily broad, although this is perhaps to be expected, because besides polarisation by rotation of the molecule as a whole parts of it can move in several different ways. Even so the spread is surprising, indicating the presence of polar groups operating under a range of restriction varying by a factor of some millions. The behaviour is probably bound up with the very strong solvent action of the butyl phthalate, this particular moulding softening at relatively low temperatures.

The effect of the addition of *cetyl palmitate*, the solute employed in the paraffin wax work previously referred to, is small (curve E, Fig. 2), the steady rise in tan $\delta$ from 50° C. upwards possibly forming part of a broad absorption curve the maximum of which was not reached. In an effort to locate such a maximum for comparison with the results of the paraffin wax work, measurements were made also at 50 cycles using a Schering Bridge but unfortunately without success.

The *β-naphthol* mixtures were studied to test the hypothesis that rotation of the hydroxyl group by itself is responsible for dielectric loss in such substances as bakelite. As anticipated, the results showed two loss maxima in the temperature curve, Fig. 3, corresponding to

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[3] W. Jackson, *Proc. Roy. Soc. A* (1935), 153, 158.

the two clearly defined modes of dipole orientation which can occur in this molecule, one, the lower temperature one, due to rotation of the hydroxyl group by itself, and the other to rotation of the molecule as a whole. A comparison of curves (A), (B), and (C), all relating to the same sample and obtained in this order, however, shows that the behaviour is more complex than this. In the specimen as first prepared the low temperature maximum is smaller, and the high temperature maximum larger, than after the " annealing " which takes place during measurement. By way of explanation, it may be suggested than in any viscous medium any equilibrium which depends upon temperature is liable to become " frozen-in " at the lower temperature, a condition which can be partially removed by annealing. Here we have such an equilibrium in the strong tendency of hydroxyl groups to associate with one another, and in the consequent molecular clustering. It may reasonably be surmised that this is the cause of the annealing effects, though it is not easy to explain them in detail, for first considerations lead one to expect rather the reverse of what is observed. Until further work has clarified the point, the explanation given above for the two maxima must therefore remain a working hypothesis, for all that the explanation preceded the discovery.

Conductivity measurements on this $\beta$-naphthol sample showed that ionic conduction was not a significant factor affecting the dielectric loss measurements.

It is of interest to consider these results in relation to dielectric materials of technical importance. It is clear from the behaviour of the chlorinated diphenyl moulding that the motion of large rigid molecules, of which chlorinated diphenyl is an example, can be effectively prevented at normal temperatures, such that in spite of their presence in appreciable concentration the loss factor can become less than $5 \times 10^{-4}$. Even so, in view of the loose places which are not to be avoided in a glass-like system, it is improbable that any plastic having markedly polar groups in it can reach the highest class of loss-free dielectrics. With materials such as bakelite, however, the chance of freezing-out polar orientation is much more remote, for even if the benzene nucleus is firmly tied down by covalencies, the hydroxyl groups will still be able to orient independently.

All organic solids with useful strength are composed of at least one-dimensionally giant molecules ; and all may be regarded as composed of one-dimensional polymers cohering in various ways. Firstly, are long molecules cohering only by weak van der Waals' forces, *e.g.* reduced rubber (an aliphatic hydrocarbon), ordinary rubber containing double bonds, and polystyrene containing phenyl groups, the two groupings of which successively increase the adhesion by increasing the polarisability though without introducing appreciable polarity. The solids which these form are rather weak ; moreover their cohesion can be overcome by thermal agitation at moderate temperatures, passing first through an elastic stage (in which rubber finds itself at room temperature) to a plastic stage before reaching the decomposition temperature, above 200° or so, at which covalencies are rapidly broken. One may say with reasonable certainty that no such material can be expected to retain its rigidity above 120°, the approximate asymptotic melting-point of all aliphatic homologous series.

Next, are the long molecules containing oxygen, nitrogen or halogens (*e.g.* polyesters or chlorinated rubber) where the cohesion is enhanced both with the polarity and the polarisability. These may have greater strength but they still retain their "thermoplasticity." At a third stage the chains are bound laterally by hydrogen bonds, with increased strength, as in cellulose: heat alone, without a solvent, is no longer sufficient to loosen the chains from one another without at the same time breaking them.

Finally, we have covalent binding between the chains producing three dimensional polymers, in which class the greatest strength is to be found. Since, however, neither heat nor solvent can make such a material plastic it is less easy to bring into a desired form than others. If it is to be moulded, the polymerisation must be completed *in situ*, an intermediate state in the preparation being used as a "thermosetting" plastic (*e.g.* bakelite, vulcanised rubber). Here, then, arises the difficulty: the intermediate state must contain reactive groups so that the polymerisation can go further, but it is not entirely an accident that practically all reactive groups are polar. The only important exception is the double bond, and that also requires a rather large activation energy unless sensitised by a neighbouring polar group, polymerisation through double bonds being otherwise always a chain-building chain-reaction. This may serve to explain why as yet there is no very strong non-polar plastic. Divinyl benzene produces a brittle incoherent polymer, though a little divinyl benzene may be added to styrene to produce a polymer free from the tendency to swell in organic solvents. Diamond is, of course, the ideal non-polar three-dimensional giant organic molecule, and suffers outstandingly from the typical defects, difficulty of shaping, impossibility of synthesis *in situ*, difficulty of obtaining sufficiently large pieces.

This work was done in the Engineering Science Laboratory at Oxford, and the authors are indebted to the inspiration of Mr. E. B. Moullin.

*The Laboratory of Colloid Science,*
*The University,*
*Cambridge.*

*The Electro-technical Laboratories,*
*The University,*
*Manchester.*

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# PROPAGATION OF TEMPERATURE CHANGES THROUGH TEXTILES IN HUMID ATMOSPHERES.

## PART I.—RATE OF ABSORPTION OF WATER VAPOUR BY WOOL FIBRES.

BY G. KING AND A. B. D. CASSIE.

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Textile fibres normally used for clothing purposes have two properties that enable them under certain circumstances to influence rate of propagation of temperature change in an important manner.[1] The two

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[1] Cassie, Atkins and King, *Nature*, 1939, 143, 163.

properties are the hygroscopic nature of the fibres, and their large surface volume ratio. The first makes possible exchange of water vapour between the fibres and an air-water vapour atmosphere. Absorption and desorption are accompanied by comparatively large evolution and absorption of heat, and if the exchange of water vapour takes place sufficiently rapidly, the resultant heat changes can influence propagation of temperature change to a marked degree. The large surface-volume ratio enables the exchange to occur rapidly enough for this to be true.

Part I of the present publication deals with the large surface-volume ratio of the fibres, and describes experimental work which shows how very rapidly wool fibres come to equilibrium with any change in water vapour conditions. Part II gives the theory of propagation of temperature change, and Part III shows its confirmation by experiment.

## Diffusion of Water Vapour into a Wool Fibre.

The radius of an average wool fibre may be taken as 10 $\mu$, or $10^{-3}$ cm., so that 1 c.c. of wool fibre has a surface area of roughly 2000 sq. cm. This large surface-volume ratio means that even if diffusion determines the time for the fibres to come to equilibrium with changed water vapour conditions, this time will be small. The diffusion constant for water in keratin is not known, but if we assume a value as small as $10^{-5}$ cm.$^2$/sec., the time required for a wool fibre to come within 80 % of its equilibrium value when water vapour conditions are changed, is roughly $10^{-2}$ sec. Thus there seems ample margin for the time interval for water vapour exchange to be small enough to enable heat of absorption to play an important part in rate of propagation of temperature change.

## Heat of Absorption and Pick-up of Water Vapour by Wool Fibres.

Trouton [2] remarked that textile fibres appear to absorb water vapour vigorously. This is consistent with the rough discussion in the previous paragraph; but his remark seems to have been overlooked, and later papers [3] have ascribed various apparent slow rates of absorption and desorption to surface forces. These apparently slow rates are due to diffusion in the surrounding atmosphere and to the effect of heat of absorption on the absorption itself. The present paper describes an attempt to measure the rate of absorption of water vapour by the fibres when the complicating influences of diffusion and heat of absorption are eliminated, or allowed for. The results show that slow rates of absorption by textiles are entirely due to external factors and have no relation to the surface structure of the colloids.

## Experimental.

Diffusion of water vapour through any surrounding atmosphere was eliminated by making the experiments *in vacuo*. The general layout is shown in Fig. 1. The wool sample under investigation, W, is suspended from a spiral spring A. The extension of this spring measures the weight of water absorbed by the wool. Other factors that must be measured are the temperature of the wool and the water vapour pressure in the apparatus; the first is measured by a length of fine platinum wire wound

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[2] Trouton, *Proc. Roy. Soc., A*, 1906, 77, 292.

[3] Fisher, *ibid.*, 1923, 103, 139.

in with the wool, and the second by the diaphragm manometer C and U-tube D.

Distilled water which had recently been boiled was introduced through the dropping funnel K. A few c.c. were run into G, and remaining air was removed by freezing the water and pumping out the system. The water was then distilled into H to remove last traces of air. B acts as a reservoir for water vapour. It has a capacity of 2 litres and holds enough water vapour to give the wool sample a water content of 10 %. This reservoir prevents cooling effects due to evaporation of water from H on opening T from causing a marked variation in water vapour pressure. Actually, it was found that on opening T the vapour pressure rose to 23·5 mm., the saturation pressure at the thermostat temperature of 25° C., and remained constant at this value.

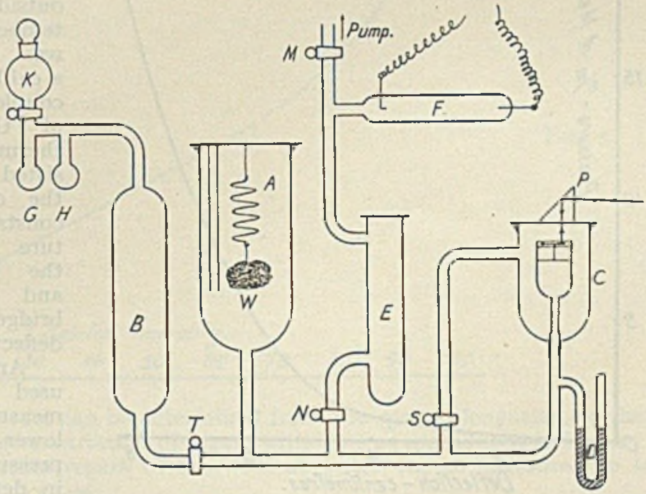

FIG. 1.

The sample consisted of about 0·25 gm. of Australian merino wool sliver, the average fibre diameter being 21 $\mu$. Grease was removed by treatment in a soxhlet apparatus. It was intimately intertwined with about 16 cm. of No. 50 S.W.G. platinum wire, and wound into a loose bundle with roughly 0·5 cm. of each end of the wire exposed. This bundle was attached to the spiral spring A, the extension of which was measured by a travelling microscope.

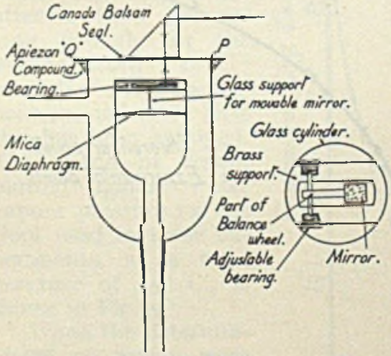

FIG. 2.

The platinum wire and its leads formed one arm of a Wheatstone bridge. The other arms were of manganin wire each of resistance approximately equal to that of the coil (35 ohms); a low resistance rheostat in one of the arms was used for final adjustment of the balance. After balancing the bridge at thermostat temperature, the galvanometer deflection was used to measure rise in temperature. The galvanometer was critically damped, and a resistance of 2000 ohms in series with the battery prevented any appreciable heating of the resistance thermometer by the bridge current. The resistance thermometer was calibrated *in situ* in the wool sample with an atmosphere of water vapour at 23·5 mm.

pressure. This was done by enclosing the sample in a closed copper cylinder in the chamber A, leaving as nearly as possible the same amount of exposed leads as in an experimental run. The cylinder was heated by a coil wound on the outside, and the temperature inside was measured by a calibrated thermocouple. Calibration of the resistance thermometer consisted of heating the cylinder to a constant temperature measured by the thermocouple, and noting the bridge galvanometer deflection.

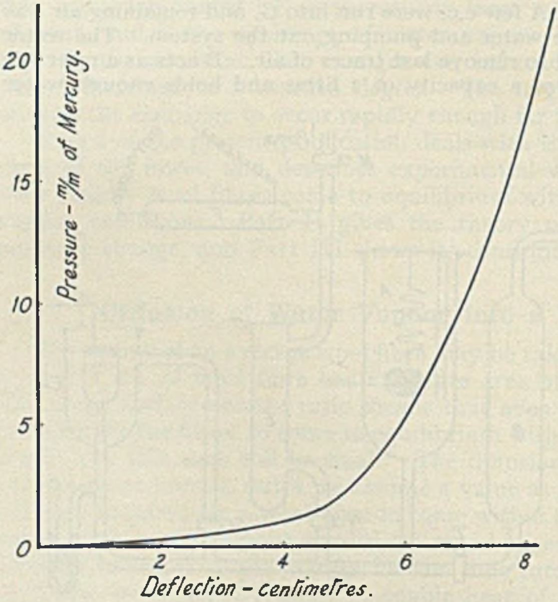

Fig. 3.

An aneroid gauge used to facilitate measurement of the lower water vapour pressures is shown in detail in Fig. 2. It was adapted from that described by Stewardson.[4] The tilting system was made more robust by replacing the knife edge with the bearing of a small clock balance wheel. The gauge itself is fitted into its enclosure by a ground joint and may easily be removed for adjustment or calibration by removing the glass plate P. The sensitivity curve is shown in Fig. 3.

The whole system, including the resistance thermometer bridge, was housed in a large air thermostat which was maintained at 25° C. ± 0·2° C. by means of a vapour pressure control and mat electric heaters spaced regularly round the walls. Two fans in the roof gave a vigorous air circulation.

Experimental procedure was as follows. The resistance thermometer leads were disconnected and the system pumped out until the wool showed a constant weight. The tap T (Fig. 1), which could be operated

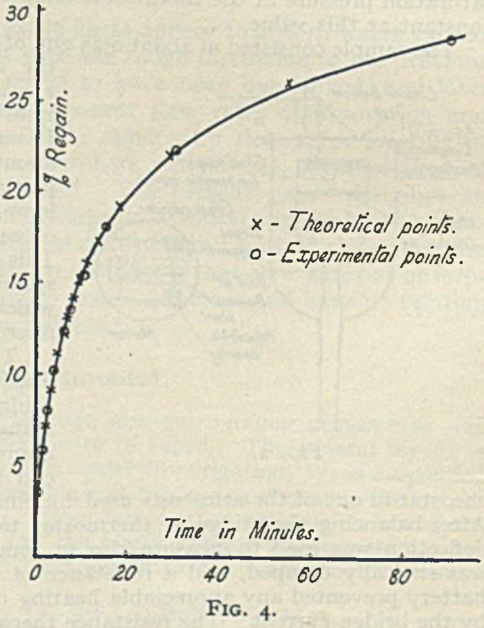

Fig. 4.

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[4] Stewardson, *J. Sci. Inst.*, 1930, 7, 7.

from outside the thermostat, was opened and the increase in length of the spring was read off at subsequent time intervals up to 90 minutes. The regain * of the wool can be determined from the spring elongation, so that these readings give variation of regain with time as reproduced in Fig. 4.

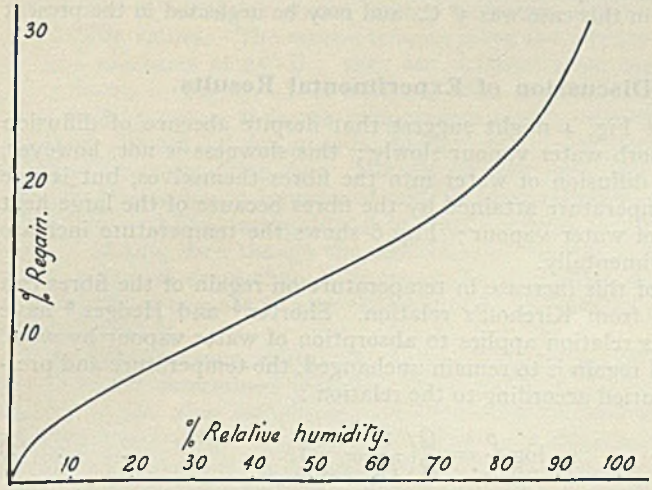

FIG. 5.

The equilibrium regain of the wool at water vapour pressures up to 23·5 mm. at 25° C. is also required. This is obtained by introducing increasing amounts of water vapour into the absorption chamber, and measuring the spring elongation and water vapour pressure after a time interval long enough for the wool to return to 25° C.: a constant water vapour pressure indicates that this has been attained. The graph of regain plotted against water vapour pressure for the wool used in these experiments, at a temperature of 25° C., is shown in Fig. 5.

When the determinations of regain were completed, the leads from the resistance thermometer were connected to the bridge circuit, and readings obtained of the temperature of the wool at successive time intervals after opening the tap T. The graph of temperature plotted against the time after opening T is shown in Fig. 6.

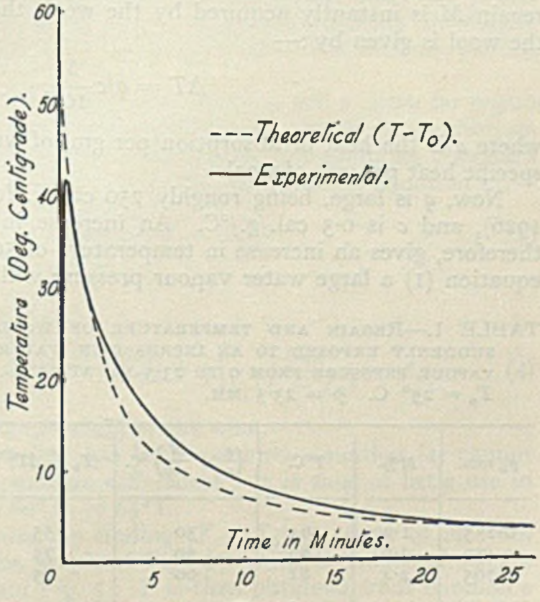

FIG. 6.

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* The percentage water content relative to the dry weight of wool.

Finally, the resistance thermometer was suspended in position, free from wool, and water vapour introduced as before ; this gave a measure of heating due to compression of water vapour in the chamber A. The rise of temperature in this case was 3° C., and may be neglected in the present experiment.

## Discussion of Experimental Results.

A glance at Fig. 4 might suggest that despite absence of diffusion wool fibres absorb water vapour slowly ; this slowness is not, however, due to a slow diffusion of water into the fibres themselves, but is due to the high temperature attained by the fibres because of the large heat of absorption of water vapour ; Fig. 6 shows the temperature increase observed experimentally.

The effect of this increase in temperature on regain of the fibres can be determined from Kirchoff's relation. Shorter [5] and Hedges [6] have shown that this relation applies to absorption of water vapour by wool. It states that if regain is to remain unchanged, the temperature and pressure must be varied according to the relation :

$$\log\frac{p}{p_0} = \frac{Q}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right), \quad . \quad . \quad . \quad . \quad (1)$$

where $Q$ is the heat of absorption per mol, $R$ is the gas constant per mol, and $T$ and $T_0$ are the absolute temperatures corresponding to $p$ and $p_0$.

Suppose a mass of wool is contained in an evacuated chamber and water vapour at a pressure $p$ is suddenly introduced. If a fractional regain $M$ is instantly acquired by the wool, the rise in temperature of the wool is given by :—

$$\Delta T = q/c\,\frac{M}{100}, \quad . \quad . \quad . \quad . \quad (2)$$

where $q$ is the heat of absorption per gm. of water vapour and $c$ is the specific heat per gm. of wool.

Now, $q$ is large, being roughly 750 cal./g. for dry wool (*cf.* Hedges, 1926), and $c$ is 0·3 cal./g./°C. An increase in regain from 0 to 2 %, therefore, gives an increase in temperature of 50° C. ; and according to equation (1) a large water vapour pressure will be required to give the sudden increase of regain to 2 % even when the fibres reach equilibrium with the water vapour instantaneously. Take the conditions of the experiment just described. Here, the wool was originally at 25° C. and water vapour at 23·5 mm. was suddenly introduced. If the temperature of the wool remained at 25° C. its regain would be more than 30 %. But rise of temperature, because of heat of absorption, makes the regain immediately acquired much less. This

TABLE I.—REGAIN AND TEMPERATURE OF WOOL SUDDENLY EXPOSED TO AN INCREASE IN WATER VAPOUR PRESSURE FROM 0 TO 23·5 MM AT 25° C. $T_0 = 25°$ C. $p = 23·5$ MM.

| $p_0$ mm. | $M$%. | $T$°C. | $\left(\frac{q}{c} \times \frac{M}{100}\right)$ °C. | $(T_0 + \Delta T)$ °C. |
|---|---|---|---|---|
| 0·235 | 1·2 | 104 | 30 | 55 |
| 0·470 | 2·0 | 89 | 50 | 75 |
| 0·705 | 2·4 | 81 | 60 | 85 |

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[5] Shorter, *J. Text. Inst. T.*, 1924, **15**, 320.

[6] Hedges, *Trans. Faraday Soc.*, 1926, **22**, 176.

initial regain can actually be determined by assuming the wool to come instantaneously to equilibrium with any water vapour and temperature conditions. Table I shows the calculation.

Column (1) contains water vapour pressures arbitrarily chosen to cover likely values. The second column gives the regains corresponding to these pressures at 25° C.: they are obtained from the experimental curve shown in Fig. 5. $T$ is obtained from Kirchoff's relation with $p$ equal to 23·5 mm.; it is the temperature giving equilibrium with the regain of column (2) for $p$ equal to 23·5 mm. The fourth column is obtained from equation (2). The regain first acquired by the wool when water vapour is introduced will be approximately that where $T$ equals $(T_0 + \Delta T)$; interpolation in Table I gives a value of roughly 2·3 %. Hence, even though the conditions of the experiment were such that a regain of more than 30 % would be ultimately acquired by the wool, it cannot because of heat of absorption increase instantaneously by more than 2·3 %.

The instantaneous increase of regain on opening the tap $T$ cannot be accurately determined from the graph of Fig. 4. The first observed point is 15 sec. after introducing the water vapour, and at this time the regain is nearly 4 %. The time required for the fibres to come to equilibrium with the water vapour-temperature conditions in their immediate neighbourhood must, therefore, be considerably less than 15 sec.; how much less, it is impossible to estimate.

Table I shows that the temperature of the wool should rise to roughly 80° C. Experimental observations recorded on Fig. 6 do not give a point much higher than 65° C., but as this temperature was observed 30 sec. after introduction of the water vapour, considerable cooling has clearly taken place: a temperature of 80° C. is not inconsistent with the cooling curve.

As the wool cools down its regain will increase, and a curve for regain versus time can be obtained, assuming the wool always in equilibrium with the water vapour-temperature conditions, and assuming Newton's law of cooling. In these circumstances the heat balance equation is:—

$$c\frac{\mathrm{d}T}{\mathrm{d}t} = q\frac{\mathrm{d}M}{\mathrm{d}t} - \nu(T - T_0), \qquad . \quad . \quad . \quad (3)$$

where $\nu$ is a constant.

Integration of (3) gives:—

$$c[\log(T_i - T_0) - \log(T - T_0)] + q\int_{T_i}^{T}\frac{\mathrm{d}M}{(T - T_0)} = \nu t, \qquad . \quad (4)$$

where $T_i$ is some initial temperature of the wool.

As Newton's law of cooling has been assumed, equation (4) cannot apply for very large temperature differences: it is thus of little use in the region of cooling from 80° C. to 65° C.

The integral is evaluated by finding $(T - T_0)$ in terms of $M$ from Kirchoff's relation and the graph of Fig. 5; suitable values of $M$ are chosen, and $p_0$ is read from Fig. 5; $T$ is then obtained from Kirchoff's relation. A graph of $1/(T - T_0)$ plotted against $M$ enables the integral to be evaluated. To obtain $\nu$ the calculated value was fitted with the observed value at the regain of 20 %, or 21 min. after entry of the water vapour.

The calculated values are shown in Fig. 4 for variation of regain with time. The calculated points lie very close to the observed curve, indicating that the theory is adequate for explanation of the shape of the curve. The calculated point at 26 % regain was obtained from an analytical asymptotic expression for equation (4). At regains in excess of 22 %, $1/(T - T_0)$ becomes so large that graphical integration is difficult and inaccurate. But if the relation $\mathrm{d}M = \alpha \, . \, \mathrm{d}p_0$ where $\alpha$ is a constant be assumed for $T$ constant, the integral of equation (4) becomes for small values of $(T - T_0)$ :—

$$\int \frac{\mathrm{d}M}{(T - T_0)} = \alpha \frac{Q}{RT_0^2} p \log(T - T_0). \quad . \quad . \quad . \quad (5)$$

Calculations similar to those of columns (1) to (3) of Table II give $(T - T_0)$ for any chosen values of $M$, and equation (5) can then be used to find $vt$ and $t$ ; $\alpha$ is obtained from the regain-relative humidity curve of Fig. 5.

The actual value of the emissivity which gives a fit for calculated and observed values of $M$ at 21 min. lies between 2 and $3 \times 10^{-4}$ cal./sq. cm./sec./° C. ; the area of the wool sample is difficult to estimate, so that the emissivity cannot be accurately determined, but these limits are in reasonable agreement with values quoted by Preston.[7]

Calculated values of $(T - T_0)$ are shown with the experimental curve in Fig. 6. The calculated values lie below the observed curve. The agreement is, however, as close as might be expected : the discrepancy is probably due to neglect of any temperature gradient from the centre to the surface of the wool sample. It should be noted that the time scale is much larger in Fig. 6 than in Fig. 4.

One point worth noting is the very small contribution of the specific heat of the wool to the cooling curve compared with that of the heat of absorption ; for example, after 20 min. the specific heat contribution to heat loss was only 1/16th that of the heat of absorption contribution. If there was appreciable delay in absorption of water vapour by the fibres, the large heat of absorption contribution would have made the agreement between calculated and observed values very poor.

## Conclusions.

There seems little doubt from comparison of experimental observations and the calculations made on the assumption that the fibres are always in equilibrium with the atmosphere in their immediate neighbourhood, that the shapes of regain-time curves are entirely due to the external factors of diffusion and dissipation of heat, and bear no relation to the diffusion of water into the fibres : in the experiment just described they are merely cooling curves. Quantitatively the experiment has given little data on the rate of pick up of water vapour by wool fibres except that the time to approach equilibrium must be less than 15 sec. None the less the results are very important because they show that in water vapour-temperature exchange between an atmosphere and hygroscopic textile fibres, the time required for the fibres to come to equilibrium with any change in conditions can be wholly neglected compared with the time required for dissipation of heat or diffusion of water vapour. They show, too, that contrary to deductions in various publications, nothing can be learnt of the surface structure of the fibre colloids from study of regain-time curves.

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[7] *Preston's Heat.* Macmillan & Co., 3rd edition, p. 506.

## Summary.

A study has been made of the rate of pick up of water vapour by wool fibres when water vapour alone is in contact with the fibres. The time required for the fibres to come to equilibrium with the water vapour when a change of pressure occurs is shown to be entirely dependent on the rate of loss of heat of absorption. When allowance is made for the effect of heat of absorption it is found that the fibres attain equilibrium in a time considerably less than 15 sec.; how much less cannot be estimated.

The forms of regain-time curves which have hitherto been observed are shown to be determined entirely by the external factors of diffusion and rate of heat loss, and they bear no relation to the structure of the fibre colloids.

The Authors' thanks are due to Mr. J. G. Miller for assistance with the experimental work.

# PART II.—THEORY OF PROPAGATION OF TEMPERATURE CHANGE.

By A. B. D. Cassie.

Part I of the present publication has shown that the time required for textile fibres to come to equilibrium with changed water vapour conditions is negligible compared with the time required to remove heat from the fibres to the surroundings. If the textile is immersed in an air-water vapour atmosphere, the time required for the fibres to come to equilibrium with the atmosphere immediately at the fibres will be negligible compared with the time required for transport of appreciable quantities of heat or water vapour through the atmosphere. This has been proved true for heat transport: it will also be true for water vapour transport, as the thermal diffusivity of air is very nearly equal to the diffusion constant of water vapour in air at N.T.P. These hypotheses enable much to be learnt of the propagation of temperature changes through textiles in slowly moving air-water vapour mixtures.

A recent paper by Henry[1] discussing diffusion in absorbing media, includes the mathematics required for the case where a temperature change diffuses through textiles. The present paper covers the case of air flowing through textiles under a mechanically applied pressure difference, and discusses the physical significance of the mathematical results.

## Propagation of Temperature Change when Air flows at a Uniform Velocity through a Semi-infinite Slab of Textile Fibres.

The simplest case to consider is an air-water vapour mixture flowing through a semi-infinite slab of textile fibres. The fibres are supposed conditioned at some definite temperature and water vapour concentration, and at time zero the temperature and water vapour concentration are changed in the incident air.

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[1] Henry, *Proc. Roy. Soc., A*, 1939, 171, 215.

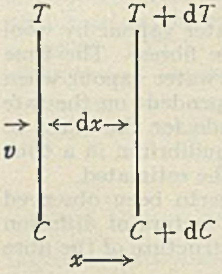

FIG. 1.

Take an element of length $dx$ in the direction of flow, and of unit cross-section normal to this direction. The equation of heat balance is :—

$$S\frac{\partial T}{\partial t} = -\rho_a c_a v\frac{\partial T}{\partial x} + q\rho\frac{\partial M}{\partial t},$$

and that of water vapour balance is :—

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} - \rho\frac{\partial M}{\partial t},$$

where $S$ is the heat required to raise the temperature of 1 c.c. of the air-textile mixture through 1° C., assuming no water vapour exchange, $\rho_a$ the density of air, $c_a$ the specific heat of air at constant pressure, $q$ the heat of absorption of 1 gm. of water by the textile, $\rho$ the mass per c.c. of textile fibres, $M$ the fractional regain of the fibres, $C$ the water vapour concentration. $M$ is assumed to vary linearly with $T$ and $C$ (*cf.* Henry [1]), so that :—

$$\frac{\partial M}{\partial t} = \sigma\frac{\partial C}{\partial t} - \omega\frac{\partial T}{\partial t}, \quad . \quad . \quad . \tag{1}$$

where $\sigma$ and $\omega$ are constants. The compressibility of the air is neglected.

Substituting this in the two equations and rearranging, gives :—

$$v\frac{\partial T}{\partial x} + \frac{S}{\rho_a c_a}\frac{\partial T}{\partial t} - \frac{q\rho}{\rho_a c_a}\left[\sigma\frac{\partial C}{\partial t} - \omega\frac{\partial T}{\partial t}\right] = 0,$$

and

$$v\frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \rho\left[\sigma\frac{\partial C}{\partial t} - \omega\frac{\partial T}{\partial t}\right] = 0,$$

or

$$V\frac{\partial T}{\partial x} + \frac{\partial T}{\partial t} - \alpha\frac{\partial C}{\partial t} = 0\ . \quad . \quad . \quad . \quad . \tag{2}$$

and

$$W\frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} - \beta\frac{\partial T}{\partial t} = 0, \quad . \quad . \quad . \tag{3}$$

where

$$V = \frac{v}{(S + q\rho\omega)/\rho_a c_a}\,;\ \alpha = q\rho\sigma/(S + q\rho\omega).$$

$$W = \frac{v}{(1 + \rho\sigma)}\,;\ \beta = \rho\omega/(1 + \rho\sigma).$$

Equations (2) and (3) can be solved by the method of normal functions. Multiply (2) by $r/V$ and (3) by $s/W$ and add ; the result is :—

$$\frac{\partial}{\partial x}\left(rT + sC\right) + \frac{\partial}{\partial t}\left\{\left(\frac{r}{V} - \beta\frac{s}{W}\right)T + \left(\frac{s}{W} - \alpha\frac{r}{V}\right)C\right\} = 0. \quad . \tag{4}$$

This can be written as :—

$$u\frac{\partial f}{\partial x} + \frac{\partial f}{\partial t} = 0, \quad . \quad . \quad . \quad . \tag{5}$$

where

$$f = (rT + sC), \quad . \quad . \quad . \quad . \tag{6}$$

and $u$ is given by

$$\left(\frac{1}{u} - \frac{1}{V}\right)\left(\frac{1}{u} - \frac{1}{W}\right) = \frac{\alpha\beta}{VW}. \quad . \quad . \quad . \tag{7}$$

Equation (7) shows that there are two values of $u$, $u_1$, and $u_2$, say, and there are two functions of the form $f(x, t)$ given by (5). The function $f(x, t)$ according to equation (5) must be of the form :

$$f(x, t) = g(x - ut). \quad . \quad . \quad . \quad (8)$$

This means that there are two linear combinations of $C$ and $T$ which are propagated unchanged in form through the textile with velocities $u_1$ and $u_2$.

Let the functions be $f_1$ and $f_2$, given by :—

$$f_1 = (r_1 T + s_1 C), \text{ and } f_2 = (r_2 T + s_2 C).$$

The ordinary routine for setting up normal functions then gives :—

$$\frac{1}{r_1} f_1 = T + \frac{W}{\beta}\left(\frac{1}{V} - \frac{1}{u_1}\right)C, \quad . \quad . \quad . \quad (9)$$

$$\frac{1}{s_2} f_2 = \frac{V}{\alpha}\left(\frac{1}{W} - \frac{1}{u_2}\right)T + C, \quad . \quad . \quad . \quad (10)$$

or, solving for $T$ and $C$.

$$T = \frac{\frac{1}{r_1} f_1 - \frac{W}{\beta}\left(\frac{1}{V} - \frac{1}{u_1}\right)\frac{1}{s_2} f_2}{1 - \frac{VW}{\alpha\beta}\left(\frac{1}{V} - \frac{1}{u_1}\right)\left(\frac{1}{W} - \frac{1}{u_2}\right)}, \quad . \quad . \quad . \quad (11)$$

$$C = \frac{\frac{V}{\alpha}\left(\frac{1}{W} - \frac{1}{u_2}\right)\frac{1}{r_1} f_1 - \frac{1}{s_2} f_2}{\frac{VW}{\alpha\beta}\left(\frac{1}{V} - \frac{1}{u_1}\right)\left(\frac{1}{W} - \frac{1}{u_2}\right) - 1}. \quad . \quad . \quad . \quad (12)$$

Take the case of a textile conditioned to a fixed temperature and water vapour concentration, and suppose the air flowing through the textile to be suddenly increased in temperature by an amount $\Delta_0 T$ and the water vapour concentration by $\Delta_0 C$. The increases $\Delta T$ and $\Delta C$ for subsequent values of $(x, t)$ are, from equations (11) and (12) :—

$$\Delta T = \Delta_0 T \frac{\left(\frac{1}{V} - \frac{1}{u_2}\right)f_1 - \left(\frac{1}{V} - \frac{1}{u_1}\right)f_2}{\left(\frac{1}{u_1} - \frac{1}{u_2}\right)} + \Delta_0 C \frac{\alpha/V}{\left(\frac{1}{u_1} - \frac{1}{u_2}\right)}(f_2 - f_1), \quad . \quad (13)$$

and

$$\Delta C = \Delta_0 T \frac{\beta/W}{\left(\frac{1}{u_1} - \frac{1}{u_2}\right)}(f_2 - f_1) + \Delta_0 C \frac{\left(\frac{1}{V} - \frac{1}{u_2}\right)f_2 - \left(\frac{1}{V} - \frac{1}{u_1}\right)f_1}{\left(\frac{1}{u_1} - \frac{1}{u_2}\right)}, \quad . \quad (14)$$

### Physical Interpretation of the Mathematical Results.

Equation (13) with $\Delta_0 C$ equal to zero answers the problem mathematically and can be used for numerical evaluation of propagation of temperature change. Its physical interpretation throws much light on the processes involved, and makes calculations simpler for many practical problems.

Take the case where $S = \rho_a c_a$, so that the textile is regarded merely as a water absorbing medium without otherwise influencing heat exchanges. This assumption introduces little error except in the case of $u_2$ when numerical values are used, and it makes physical interpretation of the equations much less complicated. The first point is to consider the values of $V$ and $W$ compared with $v$, the velocity of flow of air through the textile. $\sigma$ can be obtained from many known graphs of $M$ plotted against $C$ for a constant temperature. Its order of magnitude for most textiles and atmospheres common in Britain is $10^4$ c.c./g. $\omega$ can be obtained from $\sigma$ and Kirchoff's relation: for when d$M$ is zero, equation (1) gives :—

$$\omega = \sigma \frac{\mathrm{d}C}{\mathrm{d}T}, \qquad (15)$$

and Kirchoff's condition for constant regain is :—

$$\frac{1}{C}\frac{\mathrm{d}C}{\mathrm{d}T} = \frac{Q}{RT^2} - \frac{1}{T}, \qquad (16)$$

where $Q$ is the heat of absorption per mol. of water vapour, and $R$ is the gas constant per mol.

Equations (15) and (16) give $\omega$ equal to $5 \times 10^{-3}$/°C. when $\sigma$ is $10^4$ c.c./g. Further simplification of the physical discussion is obtained by assuming $\omega/\sigma$ equal to $\rho_a c_a/q$. This happens to be nearly true for normal water vapour concentrations. In this case :—

$$V = W = \frac{v}{(1 + \rho\sigma)}, \qquad (17)$$

and

$$\frac{\alpha\beta}{VW} = \frac{\rho^2\sigma^2}{v^2}. \qquad (18)$$

Substituting these values in the secular equation (7) and noting that $\rho\sigma$ is of the order of $2 \times 10^3$, gives :—

$$\frac{1}{u_1} = \frac{2}{V} = \frac{2}{W} = \frac{2\rho\sigma}{v}, \qquad (19)$$

and

$$\frac{1}{u_2} = \frac{1}{v} \ll \frac{1}{u_1}. \qquad (20)$$

Substitution of $1/u_1$, and $1/u_2$, from (19) and (20) in equation (13) for the case $\Delta_0 C = 0$ gives :—

$$\Delta T = \tfrac{1}{2}\Delta_0 T(\mathrm{f}_1 + \mathrm{f}_2) \qquad (21)$$

Equation (21) shows that the temperature change is propagated through the textile in two stages : one half the total temperature change passes through the textile at the same speed as the air, and the remaining half is propagated at roughly $2{\cdot}5 \times 10^{-4}$ times this speed.

The processes involved when air of constant water vapour concentration flows through a textile with changed initial temperature are now easily described. If the textile had zero specific heat and no hygroscopic property, the temperature change would be propagated at the speed of the air. The hygroscopic properties of the fibres are such, however, that the water vapour concentration as well as the temperature of the air must remain in equilibrium with the textile. If the temperature of the incident air is increased, the fibres also increase in temperature, and the water vapour concentration in the air must be increased by evaporation of water from the textile to maintain equilibrium. If there was no heat of desorption, this would leave the propagation unchanged. But as heat of desorption is required by the fibres, heat must be given by the air to the fibres to maintain the temperature equilibrium. Hence, the air in traversing the textile becomes cooled even though the fibres have zero specific heat. The cooling continues until the water vapour concentration is just that required for equilibrium with the textile at the temperature it assumes, and at its original regain.

Equation (21) shows that this temperature is midway between the initial and final temperatures, and the water vapour concentration in the atmosphere simultaneously increases by $\omega/\sigma$ times the temperature increase. The new conditions advance just as rapidly as the atmosphere flows through the fibres, because the atmosphere and fibres can produce the change spontaneously when $\omega/\sigma = \rho_a c_a/q$.

It is worth noting that the temperature acquired by the air and textile at this stage is determined largely by the properties of the air. Heat of absorption of water vapour by the fibres is the only factor associated with the textile, and this is roughly equal to the latent heat of evaporation of water. The textile can thus be regarded merely as a system for maintaining constant relative humidity in the atmosphere when temperature changes occur. The amount of heat required to evaporate sufficient water into 1 litre of air to maintain a constant relative humidity when the temperature is increased by 1° C. is roughly equal to the heat obtained by cooling 1 litre of dry air through 1° C. It is the equality of these two factors operating in opposition that gives a temperature equal to the mean of the initial and final temperatures ; if dry air had a greater heat capacity, the temperature attained would be nearer the final than the initial temperature.

The rate of propagation of this intermediate temperature equals the rate of flow of the air if the specific heat of the textile is zero and $\omega/\sigma$ equals $\rho_a c_a/q$. The incident air supplies the heat required for the evaporation of water vapour by dropping its temperature to the mean of the original and final values ; the air passing through the textile is adjusted by this temperature drop and corresponding increase in water vapour concentration to be in equilibrium with the textile, which it meets conditioned to the original temperature and water vapour concentration ; further heat or water vapour exchange is unnecessary, and the front between the original and intermediate temperatures moves along with speed $v$. The finite specific heat of the textile will, in practice, give a slower rate of propagation.

The regain of the textile has not changed appreciably at this stage, but it is continually losing water to the atmosphere, so that after a much longer period the regain is changed sufficiently to be conditioned to equilibrium with the incident air temperature and water vapour concentration. The assumptions made in deducing the mathematical equations imply that there is a sharp front between the regions of unchanged and changed regain: thus the slow component represents propagation of change of regain, whilst the fast one represents propagation of temperature and water vapour changes without change of regain.

The same processes are followed if concentration is increased whilst temperature remains constant: one front passes rapidly through the textile and across it roughly one half of the total concentration change occurs; the slower front follows bringing the second half of the concentration change and the total regain change. The faster front also brings with it an increase in temperature which disappears as the slower front proceeds; this corresponds with the first term in equation (14).

## Summary.

Mathematical theory is given for the propagation of temperature and water vapour concentration changes through textile materials when an air-water vapour mixture flows through the textile under a mechanically applied pressure difference. The results show that a change in temperature or concentration is propagated through the textile with a fast and a slow component. The physical significance of the two components is discussed.

# PART III.—EXPERIMENTAL VERIFICATION OF THEORY.

By A. B. D. Cassie and S. Baxter.

Part II has shown that temperature change of an air-water mixture is propagated through textiles in a peculiar and distinctive way when the water vapour concentration of the mixture entering the textile is kept constant. A thermocouple measuring the temperature in the bulk of the textile should show a rapid increase to a temperature roughly midway between the initial and final values; thereafter the temperature should remain constant for a considerable period, after which it should rise rapidly to the final value.

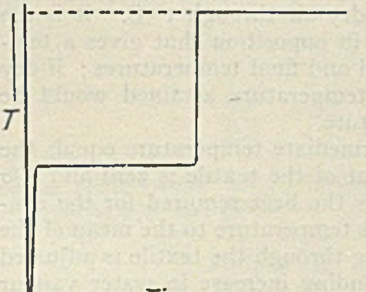

Fig. 1.

The graph for the ideal case discussed mathematically in Part II, is shown in Fig. 1. There are various simplifying assumptions in the theory, but the most important one which cannot be allowed for experimentally is that all the air passes through the textile with one velocity, $v$. This condition cannot be maintained, for flow through textiles always gives rise to channelling and a distribution of velocities. Again, the theory assumes that the air flows in parallel straight lines through the textile, whereas the actual path must be zigzag, giving a distribution of path lengths between any two planes normal to the general direction of movement of the air. The effect of varying velocities and path lengths will be to round off the sharp curve shown in Fig. 1. The distinctive features of the curve should, however, be well maintained in any experimental results, and these should readily show whether or not the theory is correct.

## Experimental.

The only precaution necessary in the experimental design is avoidance of any large heat capacity in contact with the textile fibres. It was shown in Part II that the relative value of the heat capacity of the atmosphere and the heat of sorption is largely responsible for the shape of the temperature-time curve, and introduction of any object of appreciable heat capacity changes this relationship, and must change the shape of the theoretical curve. The test body A, B, C, D, Fig. 2, was, therefore, made entirely of textile materials apart from a thin coating of cellulose varnish over the ends A, D and B, C to prevent air streaming through the ends.

The test body consisted of two concentric starched linen cylinders with the textile fibre packed as uniformly as possible between the two. The inner cylinder was first made and a sliver of the textile wound round it: starched linen was then wound round the outside, and end caps, also of linen, were fitted. Starched linen was used so that the cylinders would keep their shape, and give surfaces independent of the actual textile fibre under investigation. The top end of the inner tube fitted a double-walled glass tube, and the seal between the two was made airtight with cellulose varnish.

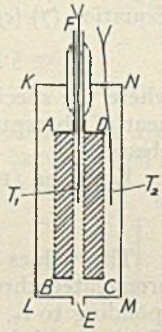

FIG. 2.

The test body was housed in a brass cylinder, K, L, M, N, and this could be immersed in either of two thermostats kept near 15° C. and 30° C., respectively. Air was passed through long spirals in the thermostats before entering the brass cylinder at E. The vapour pressure of the entering air was kept constant by bubbling one fraction of it through water maintained at the temperature of the cold thermostat, whilst the other fraction passed over $CaCl_2$. Before passing to the spirals in the thermostats the air passed over a hair hygrometer and thermometer, which checked the water vapour pressure, and through a flow-meter which checked the rate of flow.

The procedure in making a run was as follows: the brass cylinder with its textile cylinder was immersed in the cold thermostat and coupled to the spiral in that thermostat. Air from the flow meter was coupled to the other end of the spiral. The air was allowed to flow through the test body and escaped at F until the thermo-couples $T_1$ and $T_2$ showed identical temperatures. When these thermo-couples show the same temperature, the fibres must be in equilibrium with the air-water vapour mixture at the lower temperature and at the chosen water vapour pressure. The brass cylinder was then transferred to the warm thermostat and the air flow coupled to the spiral in this thermostat. Readings were made of $T_1$ and $T_2$ at convenient intervals after the beginning of the air flow through this thermostat.

## Experimental Results and their Interpretation.

The theory of Part II has been worked out for a semi-infinite slab of textile material, whilst the test pieces formed concentric cylinders. It is easily proved by using cylindrical co-ordinates that the same formulæ hold if the velocity of the gas is put equal to the volume traversing per second unit area of the cylinder whose radius is the mean of the outer and inner cylinders. Thus, if $a$ and $b$ are the radii of the inner and outer cylinders, the velocity of the gas is obtained from the volume traversing unit area of the cylinder of radius $\frac{1}{2}(a + b)$ per second; the formulæ are then the same as for propagation through a layer of thickness $(b - a)$.

(*a*) **Wool.**—Fig. 3 shows a temperature-time curve for a cylinder of wool. The speed of the air through the cylinder of radius $\frac{1}{2}(a + b)$ was 1·4 cm./sec., and $(b - a)$ was 1 cm. The water vapour pressure was 11 mm., and the temperature of the cold bath was 17·1° C. Curves (A) and (B) show respectively the temperature of the air before and after traversing the wool. The general shape of (B) is as theory predicts.

The relative humidity of the air traversing the wool varies from 75 % at the lower temperature to 32·5 % at the higher temperature, 31° C. The appropriate values of $\sigma$ and $\omega$ are $10 \times 10^3$ c.c./g., and $6{\cdot}5 \times 10^{-3}$/°C., respectively. The density of the wool in the cylinder was 0·10 g./c.c. Equation (7) (*cf.* Part II) gives for this case :—

$$u_1 = 5{\cdot}7 \times 10^{-4} \text{ cm./sec.}; \text{ and } u_2 = 1{\cdot}4 \times 10^{-2} \text{ cm./sec.}$$

where the specific heat of the wool is taken as 0·35 cal./g./°C., and the heat of absorption of water vapour by wool is 650 cal. per gm. of water absorbed.[1]

Equation (13) of Part II gives :—

$$\Delta T = \Delta_0 T(0{\cdot}62\mathrm{f}_1 + 0{\cdot}38\mathrm{f}_2) \quad . \quad . \quad . \quad (1)$$

The values of $u$ show that two fronts of temperature change are propagated through the wool: one at speed $1{\cdot}4 \times 10^{-2}$ cm./sec., corresponding to $\mathrm{f}_2$, and another at $5{\cdot}7 \times 10^{-4}$ cm./sec., corresponding to $\mathrm{f}_1$. The value of $(b - a)$ in the test piece was 1 cm., so that the times required by the fronts to traverse the wool are 70 sec. and 30 min. The total temperature change, $\Delta_0 T$, was 13·9° C. and according to equation (1), 5·3° C. should be associated with the faster front, and 8·6° C. with the slower front. The break in the temperature-time curve should thus appear at 22·4° C. This is verified with surprising accuracy by the experimental curve of Fig. 3.

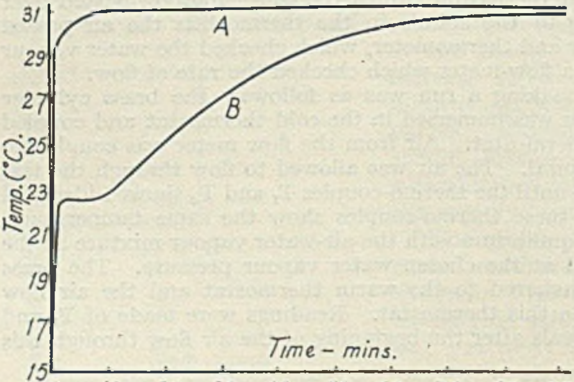

Fig. 3.—Wool, Density 0·10 gms./cc. Water vapour pressure = 11 mm. *A*.—Air temperature before passing through a cylinder of wool. *B*.—Air temperature after passing through a cylinder of wool.

The time of 70 sec. required for the faster front to pass through the cylinder is rather small for accurate measurement, as roughly 1 min. is required for the entrant air to attain its equilibrium value. 70 sec. actually fits the experimental curve well, but this agreement should not be regarded as more than qualitative. The calculated value is also liable

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[1] Hedges, *Trans. Faraday Soc.*, 1926, **22**, 178.

to error as it is given by the difference of two nearly equal quantities, neither of which is accurately known.

The slower front can be followed quantitatively, as is shown by curve (B), Fig. 3. It has the general shape predicted by theory. Lack of sharpness in this curve is most likely due to a distribution of air speeds through the cylinder. This hypothesis can be tested in the following way. If f $(v)$ be the velocity distribution in the air passing through the cylinder, it will also be the distribution of the speeds of the front; for $u_1$ is directly proportional to $v$. At any time, $t$, the fraction of air issuing from the cylinder at the higher temperature is :—

$$F = \int_{\infty}^{(b-a)/t} \mathrm{f}(u_1)\mathrm{d}u_1 . \quad . \quad . \quad . \quad . \qquad (2)$$

The temperature of the issuing air will be :—

$$T = (22{\cdot}4 + 8{\cdot}6F)^\circ \text{ C.}$$

or $F$ varies linearly with $T$. Hence, if $T$ be plotted against $(b - a)/t$, the curve will be the integral of the velocity distribution curve. This is done on curve (A), Fig. 4, for the present case of $(b - a)$ equal to 1 cm. The slopes of this curve give (B), Fig. 4. The curve is not symmetrical; that for cotton (Fig. 6B) gives a much better form of distribution curve. The curve for wool may be distorted because regain plotted against temperature for a constant water vapour concentration departs considerably from the linear relation assumed in the theory of Part II. Another factor may be the packing of the wool sliver: cotton, because of its less rigid fibres, packs more easily and more uniformly.

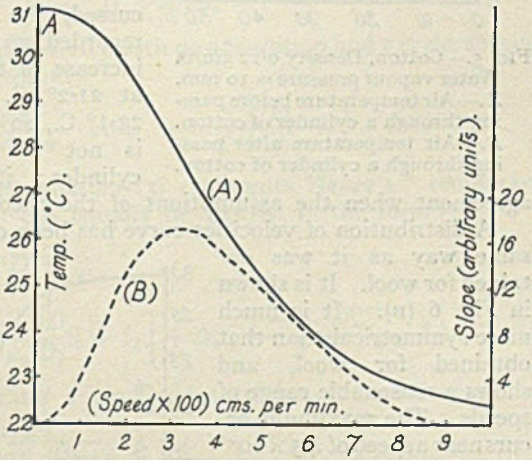

Fig. 4.—Distribution of air speeds through wool cylinder and the integral of distribution curve.

The maximum of curve (B), Fig. 4, lies around the speed $3 \times 10^{-2}$ cm./min. This gives a time of propagation of 33 min. against the calculated value of 30 min. The agreement is as good as can be expected. A correction should be applied to the calculated value to allow for expansion of the air as it passes through the cylindrical plug. The pressure difference across this was, however, only ½ mm. of Hg, and the correction is negligible.

(*b*) **Cotton.**—Similar experiments were made with cotton cylinders, and the temperature-time curve is shown in Fig. 5. Details for this experiment were :—

Density of cotton, $\rho$ = 0·12 g./c.c.
Air speed, $v$ = 1·4 cm./sec.
Cold bath temperature = 16·1° C.
Hot bath temperature = 29·9° C.

Cotton conditioned at 75 % R.H. and 16·1° C.
$\sigma = 6 \times 10^3$ c.c./g.
$\omega = 3{\cdot}9 \times 10^{-3}$/°C.
$q = 600$ cal./g. water vapour absorbed.
Cylinder wall thickness = 1 cm.

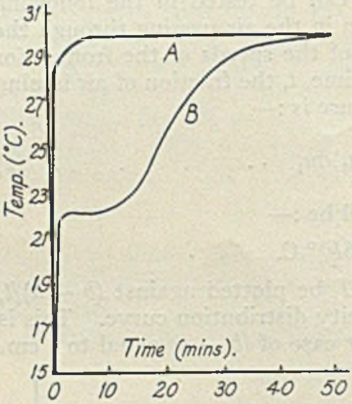

Fig. 5.—Cotton, Density 0·12 gm/u. Water vapour pressure = 10 mm. *A*.—Air temperature before passing through a cylinder of cotton. *B*.—Air temperature after passing through a cylinder of cotton.

These values give :—

$$u_1 = 7{\cdot}75 \times 10^{-4} \text{ cm./sec.};$$
$$u_2 = 1{\cdot}64 \times 10^{-2} \text{ cm./sec.}$$

and the equation for the temperature-time curve is :—

$$T = 16{\cdot}1° \text{ C.} + (8{\cdot}7f_1 + 5{\cdot}1f_2)° \text{ C.}$$

The thickness of the cylinder was again given by $(b - a)$ equal to 1 cm. The fast component should, therefore, traverse the cylinder in 61 sec. This is of the order shown by experiment, though for reasons previously discussed, the agreement can only be regarded as qualitative. The rapid increase of temperature should cease at 21·2° C. It actually ceases at 22·1° C., so that the agreement here is not so good as for the wool cylinder; it is, nevertheless, good agreement when the assumptions of the theory are recalled.

A distribution of velocities curve has been obtained for cotton in the same way as it was obtained for wool. It is shown in Fig. 6 (B). It is much more symmetrical than that obtained for wool, and shows a reasonable range of speeds. The maximum occurs near a speed of $4{\cdot}5 \times 10^{-2}$ cm./min., corresponding to a time of propagation of roughly 22 min. The time of propagation through 1 cm. given by the calculated value of $u_1$ is 21 min. The agreement is again surprisingly good.

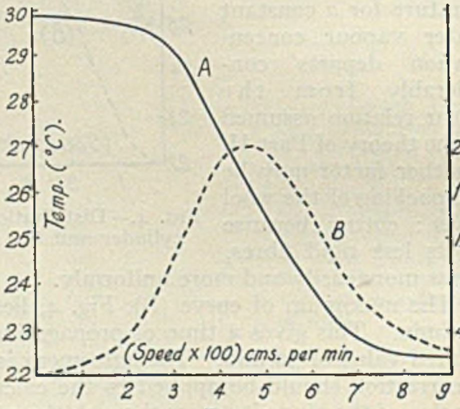

Fig. 6.

## Verification of Henry's Formulæ for Diffusion in Absorbing Media.

Henry[2] obtained formulæ for the diffusion of water vapour concentration and temperature changes into absorbing media. He found that there should be a "temporary wave" which develops quickly, and a main "wave" which develops much more slowly. His "temporary

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[2] Henry, *Proc. Roy. Soc., A*, 1939, 171, 215.

wave" increased and finally decreased to zero. Attempts to observe the "temporary wave" were unsuccessful. The conception of a temporary "wave" arises from the form in which Henry used the final diffusion equations. His formula for $\Delta T$ is :—

$$\Delta T = \Delta_0 T \mathrm{f}_2 - \frac{(1 - \mu_2{}^2 D)\Delta_0 T - \nu\Delta_0 C}{D(\mu_1{}^2 - \mu_2{}^2)}(\mathrm{f}_2 - \mathrm{f}_1), \quad . \quad . \quad (3)$$

where $\mu_1$ and $\mu_2$ are solutions of the secular equation :—

$$\left(\mu^2 - \frac{1}{D}\right)\left(\mu^2 - \frac{1}{D}\right) = \frac{\lambda\nu}{DD},$$

$D$ is given by

$$D = \frac{D''}{(1 + \rho\sigma)},$$

and $D''$ is the diffusion coefficient of water vapour through the medium without absorption.

$D$ is given by

$$D = \frac{D''}{(1 + q/c\omega)},$$

where $D''$ is the thermal diffusivity with no absorption and $c$ is the specific heat of the absorbing medium

$$\lambda = \frac{\rho\omega}{1 + \rho\sigma} \quad \text{and} \quad \nu = \frac{q/c\sigma}{1 + q/c\omega}.$$

The term $(\mathrm{f}_2 - \mathrm{f}_1)$ in equation (3) represents Henry's "temporary wave," but equation (3) can equally be written in the form :—

$$\left[1 - \frac{(1 - \mu_1{}^2 D)(1 - \mu_2{}^2 D)}{\lambda\nu}\right]\Delta T$$
$$= \Delta_0 T\left[-\frac{(1 - \mu_1{}^2)D}{(1 - \mu_2{}^2 D)}\mathrm{f}_1 + \mathrm{f}_2\right] + \Delta_0 C\frac{(1 - \mu_1{}^2 D)}{\lambda}(\mathrm{f}_1 - \mathrm{f}_2), \quad . \quad (4)$$

and the equation for water vapour concentration change becomes :—

$$\left[1 - \frac{(1 - \mu_1{}^2)D(1 - \mu_2{}^2 D)}{\lambda\nu}\right]\Delta C$$
$$= \Delta_0 C\left[\mathrm{f}_1 - \frac{(1 - \mu_1{}^2 D)}{(1 - \mu_2{}^2 D)}\mathrm{f}_2\right] + \Delta_0 T\frac{(1 - \mu_2{}^2 D)}{\nu}(-\mathrm{f}_1 + \mathrm{f}_2). \quad . \quad (5)$$

Equations (4) and (5) are similar to equations (14) and (15) of Part II• When $\Delta_0 C$ is zero, a sudden temperature change gives a rapid and a slow component for diffusion of the temperature change into the material, just as was obtained for the air-water mixture flowing through the material.

The magnitudes of the two are again almost equal for textiles; in fact, numerical values inserted in equation (4) give, for $\Delta_0 C$ zero, for cotton at a density of 0·12 g./c.c. :—

$$\Delta T = \Delta_0 T(0{\cdot}55\mathrm{f}_1 + 0{\cdot}45\mathrm{f}_2) \quad . \quad . \quad . \quad (6)$$

Henry called $\mathrm{f}_1$ the "permanent wave," and included $\mathrm{f}_2$ entirely in $(\mathrm{f}_2 - \mathrm{f}_1)$ as a "temporary wave." This seems to us misleading as $\mathrm{f}_2$ contributes roughly as much to the permanent temperature change as does $f_1$. Similarly, for a concentration change, $f_2$ contributes as much as $f_1$, although the regain of the material depends almost exclusively on $f_1$. Equations (4) and (5) do contain terms in $(f_1 - f_2)$ which are "temporary," but they are rather different from Henry's terms; a change in temperature produces a temporary change in concentration. The significance of this concentration change has been discussed in Part II. There is an equivalent transient temperature change when concentration is varied; this has also been discussed in Part II.

Henry[2] was concerned with the diffusion of a water vapour change into a bale of cotton, and tried to verify his formulæ for this case. Unfortunately, water vapour changes are exceedingly difficult to measure in the bulk of a textile material. Changes of temperature, on the other hand, are easily measured, and give the simplest means of verifying Henry's formulæ. We have made a rough check of formula (4) with the apparatus used to check the case of the air-water vapour mixture flowing through the textile. The only change necessary to convert the apparatus for diffusion measurements was to seal the top of the central linen cylinder and allow the air-water vapour mixture to flow over the sides of the outer linen cylinder. The procedure in making an experiment was then exactly as in the previous case. The results are shown in Fig. 7, curve (B), for cotton fibres at a density of 0·12 g./c.c.

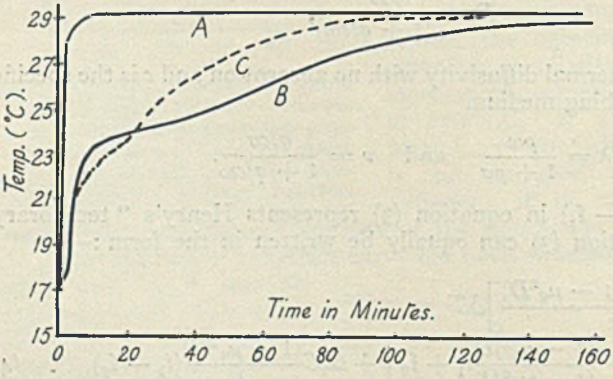

FIG. 7.—Cotton, Density 0·12 gms./cc. Water vapour pressure = 11·2 mm. *A*.—Outer air temperature. *B*.—Observed temperature at centre of cylinder. *C*.—Calculated temperature at centre of cylinder.

In this case $f_1$ and $f_2$ are solutions of the diffusion equation in cylindrical co-ordinates using $1/\mu_1^2$ and $1/\mu_2^2$ as diffusion coefficients. Hill[3] has given solutions for this equation, and their use in formula (4) gives curve C of Fig. 7. It should be noted that the time scale is much smaller in Fig. 7 than in Figs. 3 and 5.

Theory and experiment again agree on the presence of fast and slow components. The discussion given for the case of flow through the material is clearly applicable to the present case. One feature of curves (B) and (C) that might seem unexpected is that the theoretical curve is faster than the observed one. This, however, is due to the outer linen cylinder. The density of this material was 0·7 g./c.c. as compared with 0·12 g./c.c. for the bulk of the cotton. The high density would not effect the results very greatly if the air-water vapour mixture had complete access to the cotton, but only one-third of the linen mesh was open, so that constant temperature conditions could not be maintained all over the outside of the cotton. The slow observed rate of diffusion is clearly

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[3] Hill, *Proc. Roy. Soc., B*, 1928, **104**, 39.

due to this difficulty, for theory assumes that the atmosphere next the cylinder is always fully maintained at the new conditions. Apart from this, the experiment confirms Henry's formula very well, and emphasises again the very great importance of water vapour in the atmosphere for propagation of a temperature change through textiles.

The transient temperature change that occurs when $\Delta_0 C$ is finite and $\Delta_0 T$ zero was observed when conditioning the cotton cylinder before beginning an experimental run; in fact, disappearance of the transient temperature change was always used as an indication that the cylinder was properly conditioned.

## Summary.

Experiments are described which verify for wool and cotton the theory of propagation of temperature changes in textiles given in Part II.

The formulæ developed by Henry for the case of diffusion have been verified for cotton. Henry's final formulæ have been rearranged to fit more readily with their physical interpretation and with experimental results.

The authors' thanks are due to the late Dr. B. E. Atkins, who carried out the early experiments, and to Mr. F. Morris, who has assisted in all the experimental work.

The authors of Parts I, II and III wish to express their thanks to Mr. B. H. Wilsdon, Director of Research, for suggesting the investigation, and for discussion throughout the course of the work. Their thanks are also due to the Council of the Wool Industries Research Association for permission to publish this account.

*Wool Industries Research Association,*
*Torridon, Headingley,*
*Leeds*, 6.

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# THE RATE OF REACTION OF SODIUM ATOMS WITH POLYHALOGENATED METHANE DERIVATIVES.

By J. N. Haresnape, J. M. Stevels and E. Warhurst.

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Up to the present date relatively few measurements have been made of the velocity of reactions of Na atoms with organic halides which contain more than one halogen atom. The few existing measurements of Hartel, Meer and Polanyi [1] and Heller and Polanyi [2] are exclusively concerned with chlorine derivatives. These authors have measured the rate of reaction of Na atoms with the compounds of the series $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$, $CCl_4$, and found a marked progressive increase in reaction rate on passing along the series from $CH_3Cl$ to $CCl_4$. Heller and Polanyi [2]

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[1] Hartel, Meer and Polanyi, *Z. physik. Chem.*, *B*, 1933, **19**, 139.

[2] Heller and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 633.

drew attention to the fact that this increase in reaction velocity runs parallel to a decreasing force constant for the C—Cl bond. It has been shown by one of us (J.M.S.[3, 4]) that in the case of the above series, increase of the number of Cl atoms causes an increase in the atomic refractions and polarisabilities of the individual Cl atoms. Thus, this increase in polarisability runs parallel to the increase in the velocity of the reaction with Na atoms. A general method has been developed [3, 4] for the calculation of the atomic refraction of any halogen atom in any polyhalogenated methane derivative. In the case of the mixed methane derivatives containing C, H, Cl and Br certain well marked trends in polarisability of the halogen atoms are noticeable, and in view of this it is of considerable interest to measure the rates of reaction of these derivatives with sodium atoms in order to correlate trends of reaction rates with these trends in polarisability. The field chosen for investigation consisted of ten of the possible fourteen methane derivatives which contained chlorine or bromine or both halogens together. The compounds $CCl_2Br_2$ and $CClBr_3$ were omitted because of their instability and $CBr_4$ on account of its low vapour pressure; $CH_3Cl$ was also not included. In addition to these ten compounds, two methane derivatives containing F and Br, *viz.* $CHFBr_2$ and $CFBr_3$ have been dealt with, together with methyl iodide.

## Experimental.

The halides were prepared in the Physical Chemistry Department of the University of Leiden; the methods of preparation and purification are described elsewhere.[5] Two different experimental methods were employed to measure the reaction rates, (*a*) the Life Period Method [6, 7] with the modifications described recently by one of the authors,[8] and (*b*) the Diffusion Flame Method as modified by Heller.[9] In both cases the halides were used in pairs, *i.e.* in the same run the reaction rates of halides A and B were measured, and in the next run the rates of B and C, and so on. From the ratios of the rates so obtained, by choosing one halide as standard, a gradation of relative velocities along a series could be obtained. In this way the effect of errors which might vary haphazardly from run to run was eliminated as far as possible. This was essential since in some cases the difference in reaction rates is not very great. This procedure gives an accurate gradation of velocity constants, the accuracy being independent of any uncertainties in the absolute values of the constants. The purity of all the compounds was checked before use by refractive index measurements.

### The Life Period Method.

The technique employed was that which has been described for measurements of the rate of reaction of Na atoms with bromobenzene.[8] Hydrogen was the carrier gas and its rate of flow was regulated in all experiments so that $v/\delta \sim 13 \times 10^{-2}$ where $v$ is the linear streaming velocity of the carrier gas at the nozzle mouth in metres/per sec., and $\delta$ is the diffusion constant of the Na vapour in the carrier gas at the pressure in the reaction vessel ($\sim$ 3 mm.). The temperature of the Na boat was usually about 192° C. These conditions are within the range which has been shown by one of us [8] to lead to very reliable results with the Life Period Method. The majority

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[3] Stevels, *Trans. Faraday Soc.*, 1937, **33**, 1381.
[4] *Ibid.*, 1938, **34**, 429.
[5] Stevels, *Dissertation*, Leiden, 1937.
[6] Frommer and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519.
[7] Fairbrother and Warhurst, *ibid.*, 1935, **31**, 987.
[8] Warhurst, *ibid.*, 1939, **35**, 674.
[9] Heller, *ibid.*, 1937, **33**, 1556.

of the velocity constants diverged from the mean value by less than ± 10 %; in a few cases greater divergencies were obtained. In some experiments velocity constants were determined over a range of flame sizes corresponding to 14 % to 20 % absorption. No drift in the value of the constant was apparent. In the case of CHFBr$_2$ the constant was determined with a sodium temperature of 191° C. and subsequently with a temperature of 220° C., corresponding to more than a five-fold increase in sodium vapour pressure. The two sets of values were in good agreement. A typical batch of results is shown in Table I, which illustrates the points mentioned above.

TABLE I.—Reaction Vessel Temperature 255° C.

| Compound. | % Absorption of Flame. | Temp. of Sodium °C. | Velocity Constant $k(\times 10^{-12})$ cc. mol$^{-1}$, sec.$^{-1}$ |
|---|---|---|---|
| $CH_2Cl_2$ | 16·9 | 192 | 0·60 |
| | 17·0 | 192 | 0·59 |
| $CH_2ClBr$ | 15·6 | 192 | 17·8 |
| | 14·5 | 192 | 16·6 |
| | 20·8 | 192 | 16·4 |
| | 19·9 | 192 | 18·7 |
| $CH_2Br_2$ | 17·5 | 192 | 31·0 |
| | 18·0 | 192 | 31·4 |
| | 13·3 | 192 | 25·0 |
| | 14·0 | 192 | 29·8 |
| $CHFBr_2$ | 19·0 | 192 | 48·5 |
| | 21·0 | 192 | 41·7 |
| | 17·5 | 191 | 59·0 |
| | 17·2 | 191 | 57·5 |
| | 17·3 | 220 | 46·0 |
| | 19·0 | 220 | 45·0 |
| | 18·8 | 220 | 43·0 |
| $CFBr_3$ | 15·1 | 224 | 91·0 |
| | 13·9 | 224 | 89·7 |

## The Diffusion Flame Method.

The first experiments were carried out using nitrogen as carrier gas at pressures ranging from 3-15 mm., and sodium temperatures of about 240° C. The results obtained under these conditions were unsatisfactory, the velocity constants showing a pronounced decrease with increase of nitrogen pressure in the reaction vessel (see Table II).

TABLE II.—$CHClBr_2$. Reaction Vessel Temperature 250 °C.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Nitrogen pressure, $P_{N_2}$ in mm. | 2·6 | 4·0 | 4·0 | 3·9 | 5·0 | 5·1 | 7·2 | 7·5 | 11·3 |
| Vel. const. $k \times 10^{-12} \frac{\text{cc}}{\text{mol.sec.}}$ | 42 | 22 | 19 | 20 | 16 | 14 | 10·6 | 10·3 | 6·9 |

This drift of $k$ with $P_{N_2}$ was most marked for the halides which reacted fastest. The explanation of this drift lies in the fact that the flames prove to be far from ideal since they largely consisted of a central core of unreacting sodium atoms into which no halide was able to diffuse ("core" flames), because the ratio of the partial pressure of halide, $P_{Hal}$, to the sodium pressure, $P_{Na}$, at the nozzle mouth was very small ($\sim 1/3$). In order to change this state of affairs a modification in experimental technique was made. The velocity constant of the reaction is given by

$$k = \frac{\left(\ln\frac{P_{Na}}{P^0_{Na}} - \ln\frac{R}{r}\right)^2}{(R-r)^2}\,\frac{\delta}{P_{Hal}}$$

where $P_{Na}$ is the sodium pressure at the nozzle mouth, $P^0_{Na}$ the limiting pressure of sodium visible, $R$ the radius of the flame, $r$ the radius of the nozzle, $\delta$ the diffusion constant of sodium vapour, and $P_{\mathrm{Hal}}$ the partial pressure of halide in the reaction vessel. Thus, other things being equal an increase in $P_{\mathrm{Hal}}$ necessitates a proportional increase in $\delta$ for the same stationary state (*i.e.* flame diameter) to be maintained. A considerable increase in the ratio of $P_{\mathrm{Hal}}/P_{\mathrm{Na}}$ was brought about by a twenty fold increase in $\delta$. This was achieved by using hydrogen instead of nitrogen as carrier gas at very low pressures (as low as 0·4 mm.) in the reaction vessel. The correct value of $v/\delta$ was maintained by using very high speeds of flow of carrier gas ; such speeds were made possible by placing a reaction vessel on the low pressure side of three mercury vapour circulation pumps working in parallel. The tendency to form " core " flames was further reduced by lowering the sodium pressure at the nozzle mouth from $2 \times 10^{-3}$ to $4 \times 10^{-4}$ mm.

The results with the new conditions for $CHCl_2Br$, a very reactive compound, are shown in Table III, for various carrier gas pressures, $P_{H_2}$, in the reaction vessel. Although the results vary considerably, on account of increased difficulty in measuring accurately flames of such low intensity, there is no apparent drift in the value of $k$ over a more than two-fold increase in $P_{H_2}$. The value of the ratio of $P_{\mathrm{Hal}}/P_{\mathrm{Na}}$ in this case was $\sim 4$. The new value of $k$ for $CHClBr_2$ (the early results for which are shown in Table II) proved to be $180 \times 10^{12}$. On account of the decreased dazzling effect on the eye of the central zone of the resonance flames in these experiments at low Na pressures we consider that the appropriate value for $P^{0}_{\mathrm{Na}}$ is $7 \times 10^{-6}$ mm.

TABLE III.—Temperature of Reaction Vessel 250° C.

| $P_{H_2}$ in mm. | 0·43 | 0·46 | 0·46 | 0·47 | 0·54 | 0·55 | 0·55 | 0·71 | 0·94 |
|---|---|---|---|---|---|---|---|---|---|
| $k \times 10^{-12}$ | 115 | 132 | 130 | 174 | 124 | 104 | 97·3 | 130 | 88·4 |

The results obtained by the Life Period and Diffusion Flame Methods are given in Table IV and are shown schematically in Table V. In Table V the figure underlined above each compound is the collision yield, *i.e.* the average number of collisions per effective collision ; the values are those of the Diffusion Flame Method. In calculating these collision yields the value of the collision cross-section of $3{\cdot}5 \times 10^{-15}$ cm.² given by Hartel and Polanyi [10] was used. This value is probably somewhat high for monohalogenated compounds.[8] The collision yield for methyl chloride (marked*) has been taken from the work of Heller and Polanyi.[2] The figure below each compound is the atomic refraction calculated by the method developed by one of the authors.[3, 4] In the cases of $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$ and $CCl_4$ the refractions given are per chlorine atom ; in all other cases

TABLE IV.

| Compound. | Collision Yield Life Period Method. | Collision Yield Diffusion Flame Method. |
|---|---|---|
| $CCl_4$ | 5·3 | 5·5 |
| $CCl_3Br$ | 5·3 | 1·7 |
| $CHCl_3$ | — | 50 |
| $CHCl_2Br$ | 13·5 | 4·4 |
| $CHClBr_2$ | 9·0 | 2·8 |
| $CHBr_3$ | 6·3 | 1·4 |
| $CH_2Cl_2$ | 833 | 760 |
| $CH_2ClBr$ | 28 | 26 |
| $CH_2Br_2$ | 17·0 | 13·2 |
| $CH_3Br$ | — | 135 |
| $CHFBr_2$ | 11 | — |
| $CFBr_3$ | 5·5 | 2·3 |
| $CH_3I$ | 10·6 | 11·4 |

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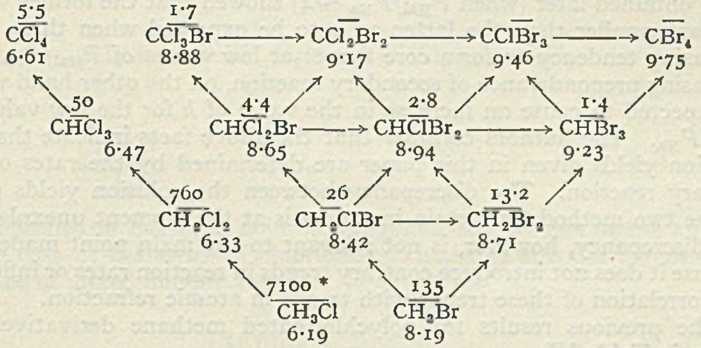
[10] Hartel and Polanyi, *Z. physik. Chem.*, *B*, 1930, 11, 97.

the refractions are per bromine atom since, in these cases, the reaction consists in the removal of a bromine atom. The values for the two series $CH_3Cl \rightarrow CCl_4$ and $CH_3Br \rightarrow CBr_4$ have been published previously by one of us.[3]

TABLE V.



## Discussion of Results.

In view of the polyhalogenated nature of these compounds the possibility of multiple reactions involving substituted radicals could not be ignored. In connection with this it was noticed that some of the compounds ($CCl_3Br$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$ and $CFBr_3$) showed a faint chemiluminescence in the early experiments with the diffusion flame apparatus, when a high nozzle pressure of sodium and a low concentration of halide were used. These chemiluminescent zones emitted the D line of sodium. It is unlikely that the primary reaction in any of these instances is sufficiently exothermic to excite the D line, since this would necessitate the assumption of improbably low values for the C—Cl and C—Br bond strengths. The luminescence is very probably due to a secondary reaction involving the halogenated radical, the heat of reaction in this case being greater than 48·3 k.cal./mol., *e.g.*

$$CCl_3Br + Na = —CCl_3 + BrNa + Q < 48{\cdot}3 \text{ k.cal.}$$

followed by

$$—CCl_3 + Na = :CCl_2 + ClNa + Q > 48{\cdot}3 \text{ k.cal.}$$

The heat change of the latter reaction may be large because it probably includes the energy change of a quadrivalent carbon atom to a divalent carbon atom (~ 37 k.cal./mol.).[11] When one of this group of halides, $CHCl_2Br$, was introduced by means of a nozzle into a large excess of sodium vapour in a " highly dilute flame " apparatus,[12] the D line of sodium was strongly emitted and a dark deposit, presumably carbon, was formed on the sides of the reaction vessel. In this case the carbon atom is probably stripped of all its halogen atoms.

If the rate of such a secondary reaction were of the same order, or faster than the corresponding primary reaction, then, in a case where the secondary reaction were occurring to an appreciable extent, the experimental value of the velocity constant would be greater than the true value for the primary reaction. This effect will arise when the value

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[11] Norrish, *Trans. Faraday Soc.*, 1934, **30**, 110 ; Heitler and Hertzberg, *Z. Physik*, 1929, **53**, 52.

[12] M. Polanyi, *Atomic Reactions*, 1932.

of $P_{\mathrm{Hal}}/P_{\mathrm{Na}}$ is small and will increase as this ratio decreases. Thus, in order to minimise the influence of any secondary reaction in the flame zones the ratio $P_{\mathrm{Hal}}/P_{\mathrm{Na}}$ was maintained as large as possible in both methods. A comparison of the early results for $CHBr_3$, $CHCl_2Br$ and $CHClBr_2$ obtained on the diffusion apparatus (when $P_{\mathrm{Hal}}/P_{\mathrm{Na}} \sim \frac{1}{4}$) and those obtained later (when $P_{\mathrm{Hal}}/P_{\mathrm{Na}} \sim 4$) showed that the former values of $k$ are smaller than the latter as is to be expected when there is an increasing tendency to form core flames at low values of $P_{\mathrm{Hal}}/P_{\mathrm{Na}}$; an increasing preponderance of secondary reaction, on the other hand would be expected to cause an increase in the value of $k$ for the low values of $P_{\mathrm{Hal}}/P_{\mathrm{Na}}$. The authors consider that the above facts indicate that the collision yields given in this paper are determined by the rates of the primary reaction. The discrepancy between the collision yields given by the two methods in certain instances is at the moment unexplained. The discrepancy, however, is not relevant to the main point made here because it does not introduce contrary trends in reaction rates or influence our correlation of these trends with trends in atomic refraction.

The previous results for polychlorinated methane derivatives are shown in Table VI.

The values given in column 4 are those obtained by the diffusion flame method in the present investigation. Although our results show appreciable divergencies from the earlier results of Hartel, Meer and Polanyi[1] the gradation of collision yields shown by our results is very close to that shown by the results of Heller and Polanyi.[2] The actual values of the collision yields are, however, a factor of 2-3 times larger than the corresponding yields given by Heller and Polanyi (col. 3).

TABLE VI.

| Compound. | Collison Yield.[1] | Collison Yield.[2] | Collision Yield. |
|---|---|---|---|
| $CH_3Cl$ | 10,000 | 7100 | — |
| $CH_2Cl_2$ | 900 | 310 | 760 |
| $CHCl_3$ | 100 | 22 | 50 |
| $CCl_4$ | 25 | 2 | 5·5 |

In a review of the diffusion flame method, Heller[9] has concluded that the range of collision yields over which the method can be used with accuracy, is 50-5000. The agreement between the results of the diffusion flame and life period methods in our experiments indicate that with the modified experimental conditions the range of the diffusion flame method can be extended to collision yields as low as ten, and perhaps five. This extension is due to the use of low carrier gas pressures (high values of $\delta$) which enable the ratio of $P_{\mathrm{Hal}}/P_{\mathrm{Na}}$ to be maintained at substantially high values even for very fast reactions, which would otherwise tend to give " core " flames.

In the schematic presentation of the results (Table V) the triangle for the halides which contain C, H, Br and Cl can be divided into a number of series by taking compounds lying along any particular straight line. The arrows indicate trends of decreasing collision yields, *i.e.* increasing reaction velocity, or increasing atomic refraction per bromine or chlorine atom as explained above. It can be seen that the whole of the results are embraced by the generalisation that an increase in atomic refraction goes parallel to a decrease in collision yields. Particular instances of this are :—

(a) $$\underset{6{\cdot}19}{\overset{7100}{CH_3Cl}} \longrightarrow \underset{8{\cdot}19}{\overset{135}{CH_3Br}} \longrightarrow \underset{13{\cdot}26}{\overset{11{\cdot}4}{CH_3I}}$$

In this case the actual reaction changes along the series; a different halogen atom is removed by the reaction in each case.

(b) In a homogeneous series, *i.e.* only one halogen involved, increase of the number of halogen atoms causes an increase in atomic refraction per halogen atom and a decrease in collision yield, *e.g.*

$$\underset{6\cdot19}{\overset{7100}{\mathrm{CH_3Cl}}} \longrightarrow \underset{6\cdot33}{\overset{760}{\mathrm{CH_2Cl_2}}} \longrightarrow \underset{6\cdot47}{\overset{50}{\mathrm{CHCl_3}}} \longrightarrow \underset{6\cdot61}{\overset{5\cdot5}{\mathrm{CCl_4}}}$$

$$\underset{8\cdot19}{\overset{135}{\mathrm{CH_3Br}}} \longrightarrow \underset{8\cdot71}{\overset{13\cdot2}{\mathrm{CH_2Br_2}}} \longrightarrow \underset{9\cdot23}{\overset{1\cdot4}{\mathrm{CHBr_3}}}$$

This parallelism has been pointed out previously by one of the authors in the case of the series of chlorides.[3] The same effect is exhibited in the case of mixed halides, *e.g.*

$$\underset{8\cdot42}{\overset{26}{\mathrm{CH_2ClBr}}} \longrightarrow \underset{8\cdot94}{\overset{2\cdot8}{\mathrm{CHClBr_2}}}$$

Presumably $\mathrm{CClBr_3}$ where there is a further increase in the atomic refraction per bromine atom, would react faster than $\mathrm{CHClBr_2}$.

(c) In the case of a series of mixed halides each containing bromine increase in the number of chlorine atoms causes an increase in atomic refraction per bromine atom and a decrease in collision yield.

$$\underset{8\cdot19}{\overset{135}{\mathrm{CH_3Br}}} \longrightarrow \underset{8\cdot42}{\overset{26}{\mathrm{CH_2ClBr}}} \longrightarrow \underset{8\cdot65}{\overset{4\cdot4}{\mathrm{CHCl_2Br}}} \longrightarrow \underset{8\cdot88}{\overset{1\cdot7}{\mathrm{CCl_3Br}}}$$

$$\underset{8\cdot71}{\overset{13\cdot2}{\mathrm{CH_2Br_2}}} \longrightarrow \underset{8\cdot94}{\overset{2\cdot8}{\mathrm{CHClBr_2}}}$$

(d) Replacement of H by F, F by Cl, or Cl by Br in a bromide results in an increased atomic refraction per bromine atom and a decreased collision yield, *e.g.*

$$\underset{8\cdot71}{\overset{13\cdot2}{\mathrm{CH_2Br_2}}} \longrightarrow \underset{8\cdot92}{\overset{11\,*}{\mathrm{CHFBr_2}}} \longrightarrow \underset{8\cdot94}{\overset{2\cdot8}{\mathrm{CHClBr_2}}} \longrightarrow \underset{9\cdot23}{\overset{1\cdot4}{\mathrm{CHBr_3}}}$$

$$\underset{8\cdot65}{\overset{4\cdot4}{\mathrm{CHCl_2Br}}} \longrightarrow \underset{8\cdot94}{\overset{2\cdot8}{\mathrm{CHClBr_2}}} \longrightarrow \underset{9\cdot23}{\overset{1\cdot4}{\mathrm{CHBr_3}}}$$

$$\underset{8\cdot42}{\overset{26}{\mathrm{CH_2ClBr}}} \longrightarrow \underset{8\cdot71}{\overset{13\cdot2}{\mathrm{CH_2Br_2}}}$$

The parallelism between the decreasing force constant for the C—Cl bonds and the increasing reaction rate, along a series $\mathrm{CH_3Cl} \rightarrow \mathrm{CCl_4}$ has already been pointed out.[2] It has also been shown that there is a progressive increase in atomic refraction of the chlorine atoms along this series.[3] Our results show that there is a parallelism between the increase

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* This value is the collision yield given by the Life Period Method.

in reaction rate and atomic refraction which extends over all the polyhalogenated methane derivatives. In the case of the series $CH_3Br \rightarrow CBr_4$ we have a further instance of a progressive decrease in force constant of the C—Br bond along the series from $CH_3Br$ to $CBr_4$.[5] It seems probable, therefore, that in all these polyhalogenated methane derivatives, increase in atomic refraction or reaction velocity will run parallel to decreasing force constants for the particular C—Hal bonds. Furthermore, it has been pointed out by Sidgwick[13] that there is a small decrease in the C—Cl bond strengths in the series $CH_3Cl \rightarrow CCl_4$, the values being 74·7, 72·5 and 72·6 k.cal./mol. for $CH_3Cl$, $CHCl_3$ and $CCl_4$ respectively. In view of this it might be concluded that the increases in reaction rate and atomic refraction also run parallel to a decrease in bond strength throughout the whole series of methane derivatives. However, there is, at present, no further bond strength data to confirm such a conclusion.

At the present moment it is not possible to deal with these parallelisms in a quantitative manner with any degree of certainty, and further clarification must await advances in the theoretical methods available for treating reactions involving such polyatomic molecules.

In conclusion, the authors wish to thank Professor Polanyi for much helpful advice during the work, Professor Van Arkel, of Leiden University, for the organic halides, and the D.S.I.R. for a research grant to one of us (J.N.H.).

*Department of Chemistry,*
*The University, Manchester.*

[13] Sidgwick, *The Covalent Link in Chemistry*, p. 121.

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# THE THEORY OF THE FORMATION OF PROTECTIVE OXIDE FILMS ON METALS, II.

By N. F. Mott.

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## 1. Introduction.

In a recent note[1] the author has suggested a theory to account for the fact that oxide films formed in air at not too high a temperature on such metals as aluminium or chromium reach a thickness of some 50 A. and then virtually stop growing, unless damaged by cracking or in some other way. The theory started from the assumption, due to Wagner, that metal ions and electrons diffuse through the oxide layer and react with the oxygen at the oxide-gas interface; and it depended on the fact that, according to quantum mechanics, electrons in a metal can penetrate a distance of the order of 50 A. into an insulating layer *without* receiving energy of excitation; in order to pass through thicker layers they must receive energy from heat motion, so that a kind of thermionic emission occurs from the metal into the oxide. The reaction is thus impossible at low temperatures for layers thicker than 50 A. The process by which electrons can pass through thin layers is known as the quantum-mechanical tunnel effect, and has been used, for instance, to account for the emission of electrons in strong fields from metals.

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[1] Mott, *Trans. Faraday Soc.*, 1939, **35**, 1175; referred to as *loc. cit.*

The aims of this paper are the following :—

(1) To show that the theory given in the paper quoted yields, at any rate for a certain range of thicknesses, a logarithmic law of growth connecting the thickness $x$ with the time $t$,

$$x = K \log (at + c) \qquad . \quad . \quad . \quad . \quad (1)$$

where $K$, $a$ and $c$ are constants. Such a law gives a negligable rate of growth above a certain thickness, which depends very little on the temperature.

(2) To make more precise the conditions under which the theory can be applied, and to show under what conditions the more familiar parabolic law

$$x^2 = \text{const.}\ t \qquad . \quad . \quad . \quad . \quad . \quad (2)$$

is to be expected.

(3) To show that under certain conditions the rate of growth given by (2) should fall off for thick films to one given by

$$x^3 = \text{const.}\ t \qquad . \quad . \quad . \quad . \quad . \quad (3)$$

(4) To apply the theory to the formation of protective films on alloys.

(5) To discuss other processes which may lead to a logarithmic law of growth.

## 2. Mechanisms for the Growth of Oxide Films.

In all the processes considered in this paper, we shall assume that metal ions diffuse through the oxide layer and react with the oxygen at the oxide-oxygen interface. We do not believe that oxygen ions, molecules or atoms diffuse *interstitially* through oxide layers, owing to their large size ; oxygen may diffuse through cracks, but such cases will be excluded from the considerations of this paper until the last section.

There are two ways in which the metal ions can move through the oxide layer :

(*a*) They can be taken into solution at the metal-oxide interface. The oxide near to the metal will then contain an excess of metal, which will be present interstitially. The concentration of metal ions will decrease towards zero as we approach the oxide-gas interface, and the concentration gradient will lead to a flow of metal ions.

(*b*) The metal is insoluble in the oxide, but the oxide can dissolve oxygen. This, for instance, is the case for the oxidation of copper. Cuprous oxide takes up excess oxygen by leaving vacant lattice positions normally occupied by copper ions. These vacant lattice points are mobile ; a copper ion can move into an adjacent vacant lattice position, and another copper ion can then move up and take its place. Thus, although oxygen is dissolved in the oxide, it is actually the copper ions that move. The vacant lattice points formed at the oxide-oxygen interface move inwards until they reach the oxide-metal interface, where they are filled up by metal ions.

Oxidation by process (*a*) will normally take place when the oxide is a "reduction semi-conductor," *i.e.* a substance whose conductivity is increased by heating *in vacuo*, whereby oxygen is driven off, leaving excess metal atoms in interstitial positions. ZnO [2] and $Al_2O_3$ [3] are

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[2] Fritsch, *Ann. Physik*, 1935, **22**, 375.

[3] Hartmann, *Z. Physik*, 1936, **102**, 709.

oxides of this type. Process (*b*) is applicable to oxidation semi-conductors, such as cuprous oxide.

In order that an oxide film shall grow it is necessary that electrons as well as ions shall pass through the oxide layer. This again can take place in various ways:

(i) By thermionic emission from the metal into the "conduction levels" of the oxide. We may denote by $\phi$ the corresponding work function. $\phi$ will *not* of course be equal to the work function of the metal *in vacuo*.[4]

(ii) By the motion of "positive holes" from the oxide-gas interface inwards. What is meant by a "positive hole" may be explained as follows: suppose that an oxygen atom takes its place in the oxide lattice at the surface, next to a metal ion which has just diffused through. Then from an ion on the surface a pair of electrons will be missing. Two electrons from a neighbouring oxide ion could move on to it. The process could be repeated; and the point from which the electrons were missing could diffuse through the oxide layer until finally filled up by electrons from the metal. A lattice point from which electrons are missing is called a "positive hole." In the interior of an oxide layer a positive hole, like an electron in the conduction layer, can move quite freely without any activation energy. But a certain energy $\psi$ will be required to move the positive hole away from the surface (cf. Fig. 1):

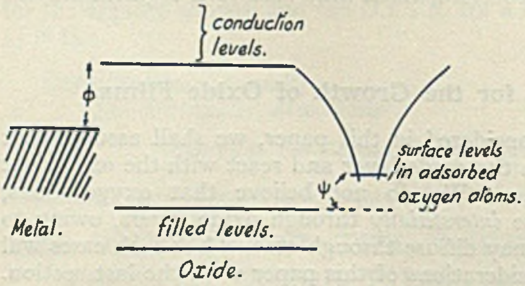

FIG. 1.—Energy levels in metal in contact with oxide layer.

(iii) As pointed out in our previous paper, electrons can penetrate a *thin* oxide layer (less than about 50 A.) without receiving the energy $\phi$ from heat motion, by quantum mechanical tunnel effect. In the same way positive holes could penetrate thin layers.

The rate of growth depends on the number $j$ of ions crossing unit area per unit time. If $\Omega$ is the volume of the oxide per metal ion, the rate of growth is given by

$$\frac{dx}{dt} = j\Omega \quad . \quad . \quad . \quad . \quad (4)$$

For the moment we shall leave out of consideration the process (iii) above. If we assume that the growth of the film is determined by the diffusion of ions and electrons from the metal to the oxygen-oxide interface, then $j$ is determined by the following equations (5), (6) and (7).

$$j = -D_i\frac{\partial n_i}{\partial x} + Fn_iv_i \quad . \quad . \quad . \quad . \quad (5)$$

$$= -D_e\frac{\partial n_e}{\partial x} - Fn_ev_e$$

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[4] *Cf.* for instance, Mott, *Trans. Faraday Soc.*, 1938, 34, 500.

Here $n_i$, $n_e$ denote the concentrations of ions and electrons at a distance $x$ from the metal-oxide interface. $D_i$, $D_e$, $v_i$ and $v_e$ denote diffusion coefficients and mobilities. The first equation gives the number of ions (assumed singly charged) and the second the equal number of electrons crossing unit area per unit time. $F$ is the field set up in the oxide which is determined by Laplace's equation

$$\frac{\mathrm{d}F}{\mathrm{d}x} = 4\pi(n_i - n_e)e \quad . \quad . \quad . \quad . \quad (6)$$

Similar equations may be written down when $n_i$, $n_e$ refer to vacant lattice points or to positive holes.

Unfortunately, general solutions of these equations have not been obtained; we shall confine ourselves to limiting cases.

We may distinguish first between *thin* films, in which the distributions of ions and electrons in the film may be calculated independently of each other, and *thick* films, in which the space charges set up if $n_i$, $n_e$ are unequal become important. We may estimate the film thickness $x$ for which the space charges become important as follows: A concentration $n$ of ions of one sign will give a field, according to (6), having a maximum value $F = 4\pi nex$. If this field is to have a negligible effect in comparison with the concentration gradient, we must have

$$Fnv = 4\pi n^2 evx \ll D\frac{\partial n}{\partial x},$$

or, writing $\partial n/\partial x \sim n/x$ and $v/D = e/kT$, we have $x \ll x_c$, where

$$x_c = \sqrt{(kT/4\pi ne^2)} \quad . \quad . \quad . \quad . \quad (7)$$

Numerical values will be given below.

We consider first, then, the behaviour of *thin* films. We shall discuss explicitly the cases where the ions and electrons pass from the metal to the oxygen-oxide interface. The theory can easily be adapted to apply to the other cases.

We denote as before by $\phi$ the work required to bring an electron from the metal into the oxide, and by $W$ the work required to bring a positive ion from the metal to an interstitial position in the oxide. Thus we may distinguish two cases:

**The case where $\phi < W$.**—It is then easier to bring electrons than ions into the oxide from the metal. There will thus be a uniform concentration of electrons in the oxide film and a concentration gradient of ions. Thus, the rate of growth is determined by the rate at which ions diffuse through the film—there being an ample supply of electrons. If $n(x)$ is the number of ions per unit volume at a distance $x$ from the metal-ion interface, the flow of ions will be given by

$$j = -\frac{\partial n}{\partial x} D_i \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The equation may be integrated subject to the conditions that $n = 0$ at the free surface and $n = n_0$ at the metal oxide interface; $n_0$ is here the concentration of metal ions in the oxide in equilibrium with the metal, and is given by

$$n_0 = N\mathrm{e}^{-W/kT} . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $N$ is the number of interstitial positions per unit volume ($N \sim 10^{22}$).

We thence obtain

$$j = n_0 D_i/x,$$

or from (4),

$$\frac{dx}{dt} = \frac{n_0 \Omega D_i}{x},$$

whence

$$x^2 = A_i t, \quad A_i = 2n_0 \Omega D_i \qquad . \quad . \quad . \quad (10)$$

A parabolic law of growth is thus obtained for all thicknesses less than $x_c$ with a rate constant $A$ which increases rapidly with temperature.

Numerical estimates of the constants involved may be of interest. We may take $N\Omega \sim 1$, $D_i \sim 10^{12}$ sec.$^{-1}$ × $(10^{-8}$ cm.$)^2 e^{-U/kT}$ where $U$ is an activation energy. Thus

$$A_i \sim 10^{-4} e^{-(W+U)/kT} \text{cm.}^2/\text{sec.}$$

If one atomic layer is added per day, $dx/dt \sim 10^{-13}$, and for a film 10 layers thick $x\, dx/dt \sim 10^{-20}$. Thus $(W + U)/kT \sim 16 \log 10 \sim 37$. If $(W + U)/kT$ is much bigger than this, practically no growth is possible.

**The case where $\phi > W$.**—There are now more ions in solid solution in the oxide than there are electrons. For very thin films (say less than 20 A.), however, the electrons will pass through the oxide layer by quantum mechanical tunnel effect as fast as they can be used up the other side to form $O^{--}$ ions; therefore the rate will be controlled by the rate of diffusion of the metal ions, and hence by (10). For thicker layers, for which the rate of penetration is very slow, the rate of growth will be controlled by the tunnel effect. As shown in our previous paper, this gives a rate of growth

$$\frac{dx}{dt} = K e^{-x/x_0},$$

where $K$, $x_0$ are constants. This, on integration, gives

$$x = x_0 \log_e \left( \frac{Kt}{x_0} + \text{const.} \right) \qquad . \quad . \quad . \quad (11)$$

We obtain thus a logarithmic law of growth.

Finally, when the rate of growth given by (11) has shrunk to very small values indeed, the rate of growth must be determined by thermionic emission of electrons followed by their *diffusion* through the oxide, and hence by an equation of the type (10), only with a much smaller value of $A$, since $n_0$ represents the electronic concentration, proportional to

$$e^{-\phi/kT}.$$

Thus, for very thin films or very thick films (subject to the limit $x < x_c$) we must always expect a parabolic law of growth; but for thicknesses of the order of 30-40 A. a logarithmic law of the type (11).

It was suggested in our previous paper that, for the oxide films formed on such metals as aluminium, chromium and perhaps zinc at room temperature, $\phi$ was so great that emission of electrons from the metal to the oxide was practically impossible, at any rate at room temperature. We thus expect for these metals an initial parabolic law of growth, giving way after a few atomic layers have been formed to a logarithmic law. The logarithmic law of growth (11) gives a practically negligible rate of thickening above a certain thickness of the order of 40 A., and this is just what is observed for those metals on which protective films are formed.

According to our hypothesis, then, the limiting thickness of protective films is due to the difficulty in getting electrons from the metal to the oxide-gas interface, rather than to the difficulty in getting ions through. This hypothesis is fully borne out by the fact that films thicker than 10,000 A. can be obtained on aluminium by anodic oxidation,[5] which shows that aluminium ions can pass through the layer if oxygen *ions* are supplied at the free surface.[6]

### 3. Detailed Calculations of Film Growth when $\phi > W$.

We shall now discuss in greater detail the constants occurring in these equations. We must first examine the parabolic law of growth, for large thicknesses, where the rate is governed by thermionic emission of electrons, in order to see how big $\phi$ must be for this process not to take place with measurable velocity. This will give a necessary condition for the formation of protective films. The rate is given by (10), namely

$$x^2 = A_e t \qquad A_e = 2n_e \Omega D_e,$$

where $n_e$ is the concentration of electrons in the oxide in equilibrium with the metal. This is given by the vapour pressure formula [7]

$$n_e = \frac{2(2\pi mkT)^{\frac{3}{2}}}{h^3} e^{-\phi/kT}$$

$$\sim 10^{19} e^{-\phi/kT} \text{cm.}^{-3}.$$

The mobility $v$ of electrons in oxides and other ionic crystals is known experimentally [8] to be of the order 100 cm./sec. per volt/cm. or $3 \times 10^4$ e.s.u., and to vary comparatively slowly with $T$. The diffusion coefficient may be deduced from the equation $D_e = kTv/e$; we obtain $D_e \sim 0{\cdot}25$ cm.$^2$/sec. With $\Omega \sim 10^{-22}$ cm.$^3$ we see that

$$A_e \sim 5 \times 10^{-4} e^{-\phi/kT} \text{ cm.}^2/\text{sec.}$$

Suppose, then, we have a layer 50 A. thick, the rate of growth is $A/2x$ or $1000 e^{-\phi/kT}$ cm./sec. The time taken to add each atomic layer is thus of the order $10^{-9} e^{\phi/kT}$ secs. If this is to be greater than, for instance, a day ($\sim 10^5$ secs.), we must have

$$\phi/kT > 14 \log_e 10 \sim 33.$$

If no growth is to take place by this process at room temperature ($kT \sim 0{\cdot}025$eV), $\phi$ must thus be greater than about 1 eV, a result already obtained by a cruder method in *loc. cit.*

We shall examine next the assumption which gives the logarithmic law of growth (11). The first assumption that we make is that an electron incident on a potential barrier of thickness $x$ and height $U$ has a chance of penetration given by the usual quantum mechanical formula [9]

$$P = P_0 \exp\{-4\pi\sqrt{(2mU)}x/h\} \qquad (12)$$

$P_0$ is a numerical factor which without sensible error may be put equal to unity. An electron will, however, only be able to penetrate the oxide

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[5] Sutton and Willstrop, *J. Inst. Metals*, 1928, 38, 259.

[6] The fact that aluminium will function freely as a cathode is probably due to the presence of cracks in the oxide, which, under cathodic conditions, are not healed up.

[7] R. H. Fowler, *Statistical Mechanics*, 2nd edn., Cambridge (1936), p. 345.

[8] Engelhard, *Ann. Physik*, 1933, 17, 501.

[9] *Cf.* for example, Dushman, *Elements of Quantum Mechanics*, p. 67.

layer from the metal if there is an oxygen *atom* the other side ready for it. Now we are assuming that the rate of growth is controlled by the penetration of electrons. Ions will diffuse through the layer and react with oxygen at the surface until the positive charge on the surface prevents further diffusion, until the arrival of the electrons. If $F$ is the field in the oxide layer, then, if there is to be no flow of ions

$$Fn_i v_i = D_i \frac{\partial n_i}{\partial x}.$$

Putting $\partial n_i/\partial x \sim n_i/x$ and $v/D = e/kT$, this gives

$$F = kT/ex.$$

The density of charge on the surface due to unpaired metal ions is $F/4\pi$, and thus the number of such ions per unit area is

$$kT/4\pi e^2 x.$$

This gives approximately the number of oxygen atoms; thus for the proportion of the surface area which can receive an electron we have

$$a^2 kT/4\pi e^2 x \quad . \quad . \quad . \quad . \quad . \quad (13)$$

($a \sim$ lattice parameter). This is about 1/3000 for layers 50 A. thick.

The probability that an electron incident on the oxide layer should penetrate it is thus given by the product of $P$ and (13). The number of electrons in the metal with energies between any limits is given by the Fermi-Dirac function. We may deduce that, if $N$ is the total number of electrons in the metal, the number passing through unit area of the layer per unit time is

$$\frac{kTu^2}{4\pi e^2 x} \frac{3N}{4\pi u^3_{\text{max}}} \int_0^\infty \mathrm{d}u \iint_{-\infty}^{\infty} \mathrm{d}v\mathrm{d}w \frac{u \,\mathrm{d}u\, \mathrm{d}v\, \mathrm{d}w}{e^{\frac{1}{2}m(u^2+v^2+w^2)/kT}+1} \quad e^{-4\pi\sqrt{\{2m(\phi-\frac{1}{2}mu^2)\}}x/h}$$

where $u_{\text{max}}$ is the maximum energy of the electrons in the metal.

The integration may be carried out in ascending powers of $T$, and gives per cm.$^2$ per sec., $Me^{-x/x_0}$, where

$$M = \frac{kTu^2}{4\pi e^2 x} \quad \frac{6N}{m^2 u^3_{\text{max}}} \quad \frac{\phi^2 x_0^2}{x^2} \left[1 + \frac{\pi^2 x^2 (kT)^2}{24\phi^2 x_0^2} \cdots \right]$$

and

$$x_0 = h/4\pi\sqrt{(2m\phi)} \quad . \quad . \quad . \quad . \quad (14)$$

To obtain the rate of growth $\mathrm{d}x/\mathrm{d}t$ we multiply by the molecular volume $\Omega$. Thus we obtain the logarithmic law (11) already given, where $x_0$ is independent of temperature, $K(= M\Omega)$ increases rather more rapidly than the first power of $T$, and also varies slowly with $x$.

As regards numerical values, if $\phi$ is expressed in eV

$$x_0 = 1{\cdot}2 \times 10^{-8}\phi^{-\frac{1}{2}} \text{ cm.}$$

As we have seen, $\phi$ must be greater than 1 eV, for protective films to be formed at all, so

$$x_0 < 1{\cdot}2 \times 10^{-8} \text{ cm.}$$

For films 50 A. thick we have for $K$ from formula (14)

$$K \sim 1 \text{ cm./sec.}$$

We may take the limiting film thickness to be that at which one atomic layer is added in a year (say $10^7$ sec.). Then $\mathrm{d}x/\mathrm{d}t \sim 10^{-15}$ and

$$x/x_0 \sim 15 \log_e 10 \sim 35.$$

For $x_0 = 1{\cdot}2 \times 10^{-8}$ cm., this gives for the maximum thickness obtainable with any value of $\phi$ large enough to give protection (viz., $\phi \sim 1$ eV),

$$x \sim 44 \times 10^{-8} \text{ cm.}$$

If $\phi$ were 4 eV, the thickness would be $22 \times 10^{-8}$ cm.

If we took for our limiting film thickness that for which one atomic layer were added in a day, we should get values of 40 and 20 A. respectively.

These thicknesses seem, as regards the order of magnitude, to be in good agreement with experiment. L. Tronstad[10] gives the following table for films which have reached a constant thickness:

| | |
|---|---|
| Mercury in dry air . . . . . . . | 15–20 A. |
| Aluminium in dry air . . . . . . . | 100–150 A. |
| Iron in dry air . . . . . . . . | 15–40 A. |
| Austenitic stainless steel . . . . . . | 10–30 A. |

In *loc. cit.*, we deduced a thickness of about 100 A. from measurements of Vernon on the increase of mass of aluminium exposed to air. Dr. Vernon has, however, pointed out to me that if we introduce Erbacher's[11] factor of 2·5 to correct for the ratio of real to apparent surface, we obtain a thickness of 40 A. in agreement with the theory.

A thickness of 40 A. for the oxide film formed on aluminium at room temperature after an exposure of a few months has also been found by Steinheil[12] from the progressive increase of transparency of evaporated aluminium films when exposed to air.

In a recent paper Vernon[13] and his co-workers have measured the rate of oxidation of zinc; below 225° C. protective films were formed, and the rate of growth satisfied approximately the equation

$$x = a \log (bt + 1).$$

Since we do not expect the logarithmic law to be valid in the early stages of growth, we cannot compare the constant $b$ in this equation with the constants of our theory. The constant $a$, which determines the limiting thickness, should, however, be very nearly equal to our $x_0$. Vernon found between 50° and 225° C. a value of about 0·08 mg./dm.$^2$, or assuming a density of unity for the oxygen in ZnO, $0{\cdot}8 \times 10^{-8}$ cm., which is the right order of magnitude ($x_0 = 1{\cdot}2/\sqrt{\phi} \times 10^{-8}$ cm., according to theory, and $\phi \gtrsim 1$ eV).

## 4. Protective Films on Alloys.

We have in this section to consider the formation of protective films on such alloys as those of iron with chromium or aluminium.

We have to note in the first place that protective oxide films can be formed at temperatures at which there is no possibility of metallic diffusion within the alloy. Therefore, when an oxide film is formed, both metals must enter into the oxide layer in the same proportion as that in which they are present in the alloy. That the constitution of the metal underneath the protective layer is the same as in the interior of the metal is also borne out by the fact that successive formations

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[10] Quoted by Evans, *Metallic Corrosion, Passivity and Protection*, p. 76 London (1937).

[11] *Z. physik. Chemie*, 1933, 63, 215.

[12] Steinheil, *Ann. Physik*, 1934, 19, 465.

[13] Vernon, Akeroyd and Stroud, *J. Inst. Metals*, 1939, 6 (advance copy).

and removals of the protective films do not alter the capacity of the metal to form the films.

On the other hand, quite small additions of a second metal are sufficient to give considerable resistance to corrosion (*e.g.* 7 per cent. of Al in iron,[14] or 3 per cent. of Al in Cu at 800° C.[15]). It is unlikely that 7 per cent. of aluminium in ferrous oxide would be sufficient to alter the work function $\phi$ of the oxide-iron interface sufficiently to prohibit the passage of electrons. We therefore suggest that initially a mixed oxide is formed, but as the film thickens the part of the film next to the metal becomes rich in aluminium (or chromium in chromium steels) until it becomes impervious to electrons, while an iron oxide film is formed *outside* it. The latter film is without influence on the protective properties.

The way in which this may be expected to happen is the following: so far we have considered the metallic ions as leaving the surface layer of the metal and moving in the oxide from one interstitial position to another until they reach the oxide-oxygen interface. Another process may possibly be occurring at the same time; a metal ion in an interstitial position may change places with a metal ion in the oxide lattice. In an oxide of a single metal this process will not have any observable effect; but in the mixed oxide the divalent ferrous ion will leave its lattice position with the expenditure of *less* energy than the trivalent aluminium or chromium ions. Therefore, in the layers next to the metal the ferrous ions will frequently be replaced by the trivalent ions, while mainly ferrous ions will succeed in penetrating to the surface and forming new oxide layers.

It may be mentioned that Fröhlich,[15] in his investigations of films of the order $10^{-4}$ to $10^{-3}$ cm. thick formed on copper and its alloys at 800° C., has found an effect of this type experimentally; he finds that alloying 2 or 3 per cent. of aluminium, beryllium or magnesium with the copper gives a very considerable protection against oxidation, the protective film being formed between the metal and the main oxide layer, and consisting predominantly of the oxide of the alloyed metal.

It should be emphasized that our theory applies primarily to oxidation at low temperatures, at which diffusion of one metal through the other is impossible. At high temperatures, on the other hand, it is possible that the proportions of the two metals in the oxide layer may be different from their proportions in the alloy. That this is the case is suggested by experiments of Iitaka and Miyake,[16] who find that the protective films formed on copper-beryllium alloys containing 1 per cent. of beryllium heated to a red heat give the electron diffraction rings characteristic of BeO alone. In order to explain these results we may assume that diffusion within the metal takes place readily, and also that the beryllium ions diffuse through the oxide layer much faster than the larger copper ions, so that a protective film of BeO is formed before any appreciable amount of $Cu_2O$ appears.

## 5. Thick Films.

So far we have considered films so thin that the space charge set up by the diffusing ions and electrons is negligible. The critical thickness,

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[14] Portevin, Pretet and Jolivet, *J. Iron Steel Inst.*, 1934, **130**, 219.

[15] K. W. Fröhlich, *Z. Metallkunde*, 1936, **28**, 368.

[16] *Nature*, 1936, **137**, 457.

if given by (7), which may be written

$$x_c = \sqrt{(kT\Omega D/\pi e^2 A)}$$

where $A$ is the constant in the growth equation. For a film that grows to $10^{-4}$ cm. in an hour, $A \sim 10^{-5}$, and, if the growth is governed by the diffusion of electrons, $D \sim 0{\cdot}2$ cm.$^2$/sec. Putting in numerical values, we obtain

$$x_c \sim 3 \times 10^{-5} \text{ cm.}$$

If the rate of growth is controlled by the rate of diffusion of positive ions, $D$ and hence $x_c$ will be smaller.

We consider, then, the limiting case of films thick compared with $x_c$.

If the film when of stoichiometric composition is a conductor (*e.g.* an ionic conductor, as are silver halides above room temperature), then no space charges can be set up, and the laws of growth are the same as for thin films. For insulators, however, since we must have no large space charge set up, we may assume that the concentration of ions and electrons is equal, except in the oxide film at a distance comparable with $x_c$ from the metal. Moreover, the constant $n_0$ which occurs in equation (10) in the formula for $A$ will no longer be $Ne^{-\phi/kT}$, $Ne^{-W/kT}$, whichever is the smaller, but $Ne^{-\frac{1}{2}(\phi+W)/kT}$. Thus, unless $\phi$ and $W$ happen to be exactly equal, the value of $A$ appropriate to thick films is greater than for thin films. We thus expect

$$x^2 = At \quad \text{(thin films)}$$

$$\frac{dx}{dt} = \frac{A^1}{2x}, \quad x^2 = A^1(t + t_0) \quad \text{(thick films)}$$

with

$$A^1 > A.$$

The plot of $x^2$ against $t$ should thus be as in Fig. 3.

There is, however, one case in which thick films should grow more slowly than thick ones. Suppose that metal ions go into interstitial positions in the oxide, but electrons are not transferred through the conduction band of the oxide, but as positive holes through the full band. This will be the case if, in Fig. 1, $\psi < \phi$. Then the diffusing particles, positive ions and positive holes, will both produce a positive space charge in the oxide.

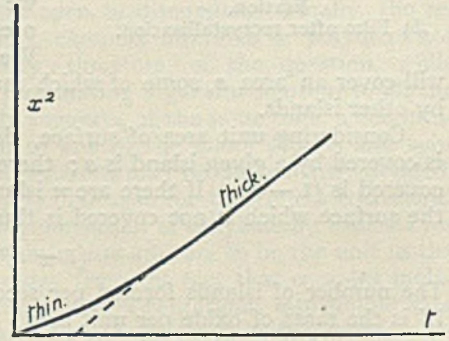

FIG. 2.—Theoretical growth law for insulating oxides.

It follows that the concentration $n$ of neither electrons nor ions can reach a value great enough to set up a field large enough to stop the diffusion of either. Since the field is proportional to $n_0 x$, we deduce that $n_0$ near a boundary, instead of remaining constant as the film thickens, decreases as $1/x$. Thus the equation governing the growth will be of the form

$$\frac{dx}{dt} = \frac{\text{const.}}{x^2}$$

or $x^3 = at + b$.

At present we do not know of any reaction to which these considerations are applicable.

## 6. A Logarithmic Law of Growth due to Recrystallisation.

Some metals, *e.g.* copper, form compact oxide films of any thickness, the rate of growth following the parabolic law. These films give interference colours at suitable thicknesses. No interference colours are obtained with the protective films on aluminium or chromium, probably because they are not thick enough. There is a third type of oxide film, such as that formed on zinc[13] above 225° C., which follows a logarithmic law of growth, but reaches much greater thicknesses ($\sim$ 500 A.) than the protective films, and whose growth rate is very sensitive to temperature. These films do not give interference colours, and show a granular structure under the microscope. It is suggested that in these cases the original compact film breaks up and recrystallises, a hypothesis confirmed by electron diffraction results due to Shearer.[17]

It may be worth while to state a set of assumptions applicable to these thicker films from which a logarithmic law can be derived. Before recrystallisation we imagine a thin film (Fig. 3(*a*)), during recrystallisation we imagine that the metal is covered by a number of islands of oxide, as in Fig. 3(*b*). We assume that at any part of the surface which is not already covered there is a probability $p$ per sec. per cm.$^2$ that an island will begin to form, and that once started it will grow rapidly to a weight $w$, which we assume to be independent of the presence of neighbouring islands. We also assume that each island will cover an area $a$, some of which may, however, already be covered by other islands.

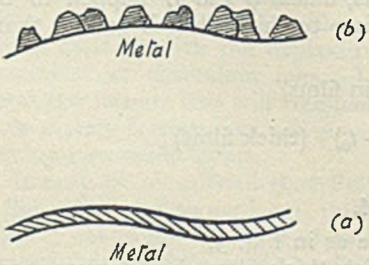

Fig. 3.
(*a*) Compact film before recrystallisation.
(*b*) Film after recrystallisation.

Considering unit area of surface, the probability that a given point is covered by a given island is $a$; therefore the probability that it is *not* covered is $(1 - a)$. If there are $n$ islands per unit area, the fraction of the surface which is not covered is thus

$$(1 - a)^n.$$

The number of islands formed per second is thus $p(1 - a)^n$, so that if $W$ is the mass of oxide per unit area,

$$\frac{\mathrm{d}W}{\mathrm{d}t} = pw(1 - a)^n.$$

But $W = nw$, so this equation becomes

$$\frac{\mathrm{d}W}{\mathrm{d}t} = pw(1 - a)^{W/w}$$

$$\sim pwe^{-Wa/w},$$

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[17] Unpublished; quoted by Vernon, e.a. *loc. cit.*

since $a$ is small, $W/w$ large. Integrating this, we obtain

$$W = \frac{w}{a}\log(pat + 1),$$

which is the required equation.

The author would like to express his thanks to Dr. W. H. J. Vernon for valuable discussions of the experimental material.

*H. H. Wills Physical Laboratory,*
*University of Bristol.*

# THE POLYMERISATION OF ETHYLENE BY ALKYL RADICALS.

By Joseph C. Jungers and Lourdu M. Yeddanapalli.

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Polymerisation reactions have long attracted attention by reason both of their scientific interest and their industrial importance. Most of these reactions, however, hardly admit of a complete theoretical treatment. In fact, the different stages in polymerisation, *viz.* formation of active centres or nuclei, development and breaking of the chain, etc., cannot be adequately explained by experimental data alone, but need also the postulation of certain hypotheses usually difficult to verify. Thus, the active centres are often supposed to be activated molecules or bivalent radicals, the existence of which has not been proved by independent methods. Again, the question whether it is the activation energy, or the steric factor that plays an important part in the progress and stopping of the chain, is still open to discussion. Finally, the reaction products are, in most cases, complex mixtures or polymers not easy to analyse. The complexity, therefore, of the question, while rendering futile any attempt at formulating a general solution to all the problems raised in polymerisation, suggests, at the same time, a delimitation of the field of investigation to one of the many groups and subgroups into which polymerisation reactions may be conveniently divided, and the choice from it of one particular case for theoretical treatment. We selected for our study the polymerisation of ethylene by radicals for a two-fold reason. First, because ethylene appears to be the unit in the building-up of radicals and molecules, from the fact that complex molecules decompose, under certain experimental conditions, into simple ones and ethylene, while simple radicals add up with ethylene to give complex ones, thus pointing to the existence of an equilibrium of the type

$$C_3H_7 \rightleftarrows CH_3 + C_2H_4$$
$$R - C_2H_4 \rightleftarrows R + C_2H_4$$

Secondly, because ethylene polymerisation, for the reason just given, offers a very good means of studying the inter-relations between different radicals from the point of view of polymerisation efficiency.

Previous researches have shown that polymerisation could be induced by free radicals from acetone, azo-methane, mercury-dimethyl, etc.[1]

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[1] See *e.g.*, Taylor and Jungers, *Trans. Faraday Soc.*, 1937, **33**, 1353.

More recently, Joris and Jungers[2] polymerised ethylene with ethyl radicals produced from ethyl iodide in the presence of mercury. The alkyl iodides exhibit in the ultra-violet an absorption band with a maximum at about 2600 A. corresponding to the dissociation of the molecule into a radical and an atom of iodine. The technique devised in the case of ethyl iodide permits, therefore, of the production of alkyl radicals for study under comparable conditions. The radicals studied in the present research are methyl, ethyl, *n*- and *iso*-propyl. Since the mechanism proposed for ethylene polymerisation is a succession of bimolecular additive reactions,

$$CH_3 + C_2H_4 \rightarrow C_3H_7$$
$$C_3H_7 + C_2H_4 \rightarrow C_5H_{11} \ . \ . \ .$$

it should be possible to verify it with the help of the above series of radicals in which the first and last members differ by a molecule of ethylene. Also, valuable information may be obtained concerning the variation of steric factor and activation energy in the course of the reaction, and the mechanism of the chain breaking.

## 1. Experimental Procedure.

The methyl and *n*-propyl iodides used were Merck's, the ethyl and *iso*-propyl, Fraenkel's products. The apparatus was, in principle, the same as that of Joris and Jungers.[2] Alkyl iodides, after being freed from all volatile impurities, were introduced into adequate vessels and were kept, when not actually in use, in liquid air to avoid decomposition or contamination by foreign products. Mixtures of ethylene and iodide, in varying proportions, could be introduced into the reaction chamber consisting of a silica tube of 3 cm. in diameter and 20 cm. in length and fitted inside with a pyrex tube having small receptacles for the mercury what is necessary to take up the iodine liberated from the alkyl iodides during the reaction. The upper end of the chamber was connected with a side tube terminating in a small bulb in which gaseous reaction products could be condensed with freezing mixtures of known temperature and analysed for methane and hydrogen. To maintain the reaction chamber at any desired temperature, it was enclosed in a cylindrical electrical furnace of thick aluminium wound round with resistance wire and provided with an aperture closed with a quartz tube permitting the entrance of light.

The source of light was a mercury arc of the Heraeus type operated at high temperature at 110 v. and 3·5 amp., the distance from the centre of the arc to that of the reaction vessel being 14 cm. For certain experiments, voltage and distance were changed to 150 v. and 10·5 cm., and 75 v. and 22 cm. respectively, the amperage remaining constant, in order to secure varying light intensities. The light was filtered through uviol glass before entering the reaction vessel.

Pressure variations were measured manometrically at room temperature. Any non-volatile products deposited on the walls of the silica vessel were burnt away at the end of the reaction at a dull red heat with a blow-pipe.

## 2. Experimental Results.

Several series of measurements were made so as to compare the efficiencies of radicals under different experimental conditions. The results are recorded in Table I. Column 1 represents the serial number of the experiment; 2, the radical under consideration; 3, 4, 5, respectively, pressure of iodide, of ethylene and pressure variation $\Delta P$ resulting from the reaction; 6, the yield, *i.e.* ratio between total pressure variation and iodide pressure

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[2] Joris and Jungers, *Bull. Soc. Chim. Belg.*, 1938, 47, 135.

$\Delta P/P_I$ ; 7, the time of half-reaction ; 8, remarks. The results are also represented graphically by plotting decrease of pressure against time. In all the experiments, the reaction was followed to completion, *i.e.* till no further

TABLE I.

| No. of Experiment. | Radical. | $P$ iodide in cm. | $P$ ethylene in cm. | $\Delta P$ in cm. | $\Delta P/P_I$. | $t_{\frac{1}{2}}$ Reaction. | Remarks. |
|---|---|---|---|---|---|---|---|
| **A.—Influence of Iodide Pressure and B, of Temperature.** | | | | | | | |
| **245° C.** | | | | | | | |
| 1 | $CH_3$ | 6·50 | 11·83 | 10·3 | 1·59 | 17′ | 0·45 ($CH_4$) |
| 2 | $C_2H_5$ | 6·50 | 12·03 | 10·1 | 1·54 | 16′ | |
| 7 | $CH_3$ | 2·92 | 12·23 | 6·00 | 2·03 | 15′ | 0·12 ($CH_4$) |
| 8 | $C_2H_5$ | 2·90 | 11·70 | 4·90 | 1·69 | 11′ | |
| 9 | $C_3H_7$ (*i*) | 3·17 | 12·03 | 2·97 | 0·95 | 6′ | |
| 3 | $CH_3$ | 1·75 | 12·08 | 3·71 | 2·12 | 13′ | 0·06 ($CH_4$) |
| 4 | $C_2H_5$ | 1·60 | 12·10 | 2·80 | 1·75 | 8′ | |
| 5 | $C_3H_7$ (*n*) | 1·90 | 12·15 | 2·28 | 1·20 | 7′ | |
| 6 | $C_3H_7$ (*i*) | 1·95 | 12·15 | 2·00 | 1·02 | 5′ | |
| **200° C.** | | | | | | | |
| 10 | $CH_3$ | 3·03 | 12·42 | 6·90 | 2·30 | 31′ | |
| 11 | $C_2H_5$ | 3·11 | 12·07 | 5·98 | 1·92 | 26′ | |
| 12 | $C_3H_7$ (*i*) | 2·97 | 12·03 | 4·00 | 1·35 | 16′ | |
| 16 | $CH_3$ | 1·89 | 12·41 | 4·60 | 2·44 | 32′ | <0·01 ($CH_4$) |
| 17 | $C_2H_5$ | 2·00 | 12·20 | 4·00 | 2·00 | 25′ | |
| 18 | $C_3H_7$ (*n*) | 1·80 | 12·15 | 3·40 | 1·89 | 22′ | |
| 19 | $C_3H_7$ (*i*) | 2·15 | 12·42 | 2·89 | 1·42 | 13′ | |
| **130° C.** | | | | | | | |
| 20 | $CH_3$ | 1·90 | 12·65 | 4·75 | 2·50 | ∼ 275′ | |
| 26 | $C_3H_7$ (*n*) | 2·03 | 12·15 | 3·88 | 1·90 | ∼ 235′ | |
| 21 | $C_3H_7$ (*i*) | 2·05 | 12·20 | 2·75 | 1·34 | 80′ | |
| **C.—Influence of Light Intensity.** | | | | | | | |
| **245° C.** | | | | | | | |
| 7 | $CH_3$ | 2·92 | 12·23 | 6·00 | 2·03 | 15′ | I |
| 14 | $CH_3$ | 3·08 | 12·20 | 7·33 | 2·38 | 50′ | III |
| 9 | $C_3H_7$ (*i*) | 3·17 | 12·03 | 2·97 | 0·95 | 6′ | I |
| 13 | $C_3H_7$ (*i*) | 2·95 | 12·02 | 3·02 | 1·02 | 14′ | III |
| **200° C.** | | | | | | | |
| 12 | $C_3H_7$ (*i*) | 2·97 | 12·03 | 4·00 | 1·35 | 16′ | I |
| 15 | $C_3H_7$ (*i*) | 3·02 | 12·03 | 3·82 | 1·26 | 10′ | II |
| **D.—Influence of Ethylene Pressure.** | | | | | | | |
| **200° C.** | | | | | | | |
| 24 | $CH_3$ | 2·10 | 6·20 | 3·52 | 1·67 | 33′ | |
| 25 | $C_3H_7$ (*n*) | 1·78 | 6·82 | 2·68 | 1·50 | 27′ | |
| 16 | $CH_3$ | 1·89 | 12·41 | 4·60 | 2·44 | 32′ | |
| 18 | $C_3H_7$ (*n*) | 1·80 | 12·15 | 3·40 | 1·89 | 22′ | |
| 22 | $CH_3$ | 2·03 | 24·75 | 6·90 | 3·40 | 32′ | |
| 23 | $C_3H_7$ (*n*) | 2·00 | 26·70 | 4·95 | 2·47 | 29′ | |

pressure variation took place. It is, therefore, from experimentally observed changes of pressure that the yields have been calculated. Yields have been chosen to evaluate the polymerisation efficiencies of radicals, as they eliminate the factor of the slight pressure variations unavoidable in a series of experiments.

### A. Influence of Iodide Pressure.

The effects produced on polymerisation yields by variations in iodide pressure, at an approximately constant pressure of ethylene, have been studied. The experimental data are recorded in Table I A and B, and represented by Figs. 1 *a*, *b*, *c*, from which the following conclusions may be drawn. The yield, at a given pressure, decreases down the series of iodides methyl, ethyl, *n*- and *iso*-propyl. This is to be ascribed to the difference in the steric factors of these radicals, as will be explained in detail in the discussion. Secondly, for any radical, the yield increases with decreasing iodide pressure. This may be explained in the following manner. The radicals can react not only with ethylene molecules present but also among themselves, and since this latter reaction increases in importance at higher

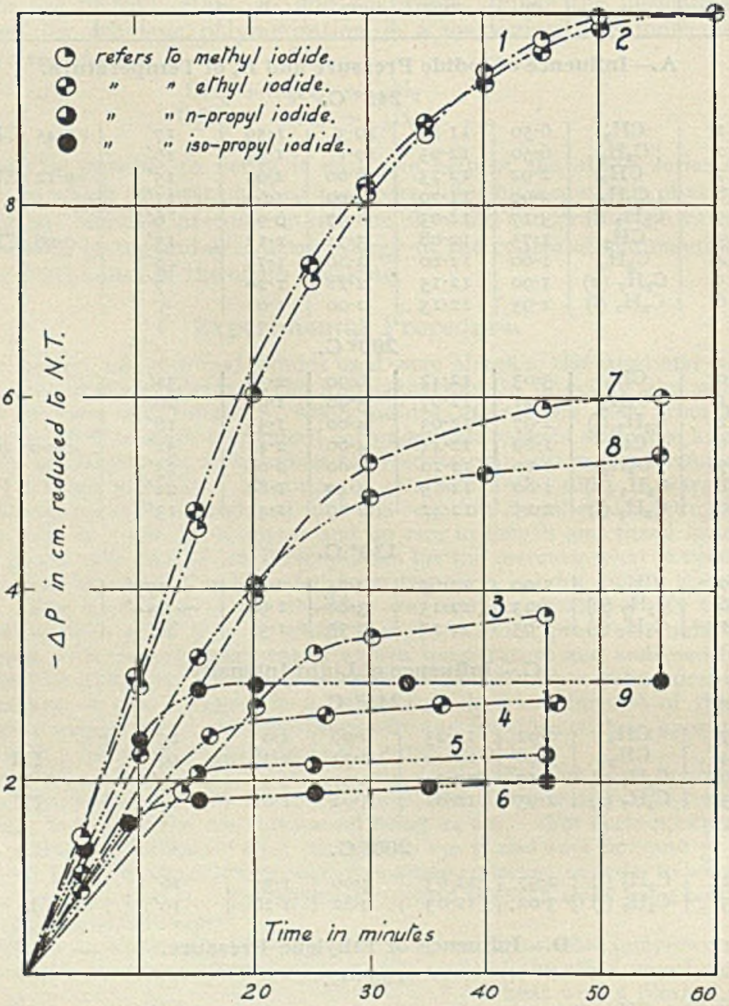

FIG. 1*a*—Polymerisation of Ethylene at 245° C.

radical concentrations brought about by higher iodide pressures whilst the ethylene radical reaction decreases, the polymerisation yield decreases at higher iodide pressures. At lower iodide pressures, on the contrary, the mutual radical combination is favoured less than the main ethylene polymerisation reaction ; the more so as the relative concentration of ethylene becomes proportionately greater, and consequently the yield increases. In agreement with this the yield undergoes a further increase when the relative pressure of ethylene is raised still more as in the experiments recorded in Table I D. Finally, the relative differences in yields for the several iodides increase with decreasing iodide pressure, and tend to limiting values at low pressure, near about 2 cm., as may be seen in the case of methyl and ethyl iodides at 245° C. This limiting region of iodide pressure is of particular importance for the study of the specific influence of the individual radicals in the polymerisation of ethylene, because since they are at such a low pressure, in very dilute concentrations, they undergo much less mutual combination and contribute more effectively to polymerisation, each furnishing its characteristic yield. For this reason, experiments were carried out in that iodide pressure region with increasing ethylene pressures, the results of which will be given later.

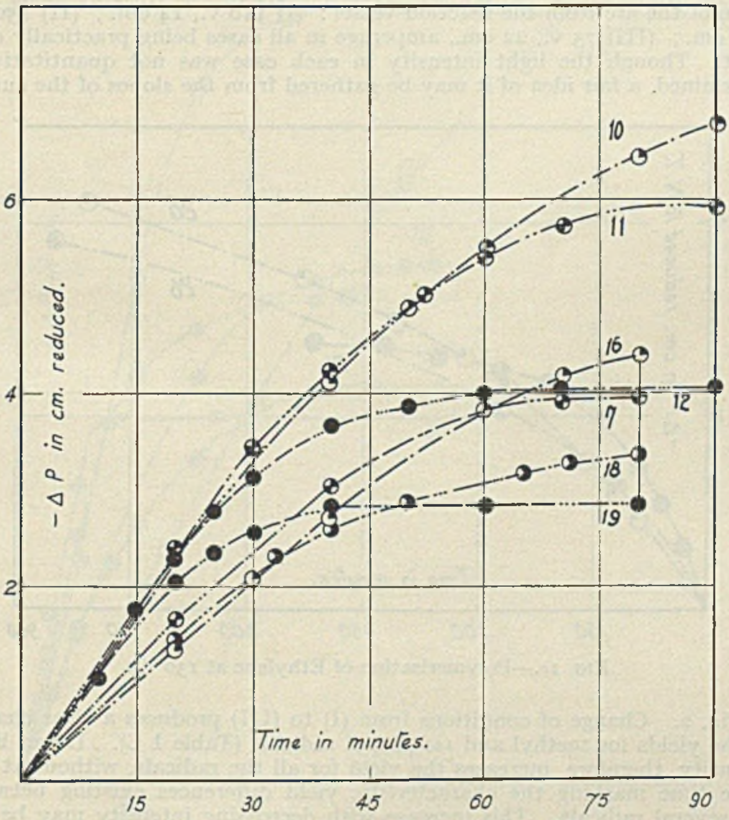

FIG. 1*b*.—Polymerisation of Ethylene at 200° C.

Here it should be added that only in the case of methyl iodide is there evidence of formation of methane, becoming appreciable at higher iodide pressures and temperatures (see column 7 of Table I A, B), although it is, even under these conditions, negligible with what was obtained by Taylor and Jungers [1] when using acetone as sensitiser.

### B. Influence of Temperature.

Experiments made at 245, 200 and 130° C. show that the behaviour of radicals just described is little modified by temperature variation, except that the yield for all of them increases slightly with lowering temperature. The reason for this is that the radical concentration is slightly smaller at lower temperature due to a lower rate of iodide decomposition and, as was pointed out in the preceding section, a lower radical concentration favours the yield.

### C. Influence of Light Intensity.

To examine the influence of light intensity on yields, experiments were conducted with varying intensities by modifying the voltage and the distance of the arc from the reaction vessel : (I) 110 v., 14 cm. ; (II) 150 v., 10·5 cm. ; (III) 75 v., 22 cm., amperage in all cases being practically constant. Though the light intensity in each case was not quantitatively determined, a fair idea of it may be gathered from the slopes of the curves in Fig. 2. Change of conditions from (I) to (III) produces a clear change in the yields for methyl and *iso*-propyl radicals (Table I C). Lower light intensity, therefore, increases the yield for all the radicals, without at the same time masking the characteristic yield differences existing between the several radicals. This increase with decreasing intensity may be explained in terms of a lower radical concentration, as in the preceding sections.

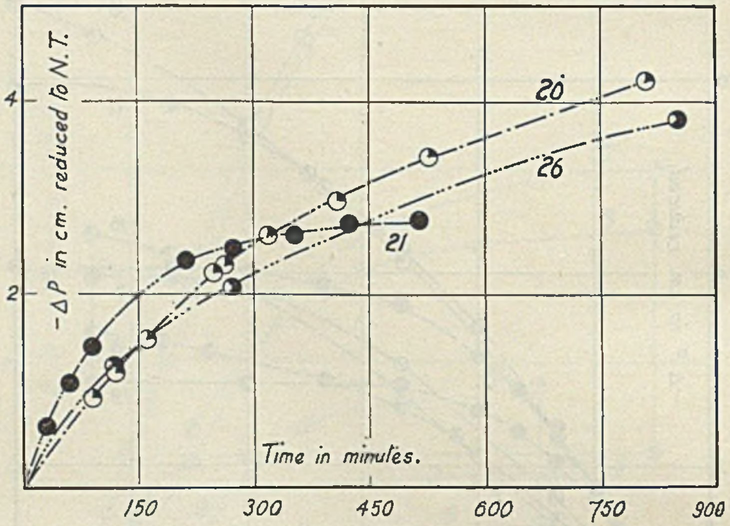

FIG. 1*c*.—Polymerisation of Ethylene at 130° C.

### D. Influence of Ethylene Pressure.

In the acetone photosensitised polymerisation of ethylene, Taylor and Jungers [1] observed that the yield increased with ethylene pressure and that at a constant acetone pressure of 1·3 cm. it reached a limiting value when ethylene was about 25 cm. pressure. With a view to studying the behaviour of our radicals up to this limiting pressure of ethylene, experiments were made with methyl and *n*-propyl iodides at that iodide pressure at which, as mentioned in sec. 2A, the relative yield differences for radicals were tending to a limit, *viz.* at about 2 cm. pressure. From the experimental data in Table I D, it is obvious that the yields for both radicals increase with ethylene pressure, and in the neighbourhood of 25 cm. ethylene pressure, the yield for the methyl is 3·4 and for the *n*-propyl radical 2·47, the difference being nearly unity. This means that the methyl radical has been able to add on one ethylene molceule more than *n*-propyl ; but the fact that the two radicals differ in structure also by one ethylene molecule, leads us to believe that the polymer in either case is similar in form and results from a direct addition of ethylene molecules to radicals.

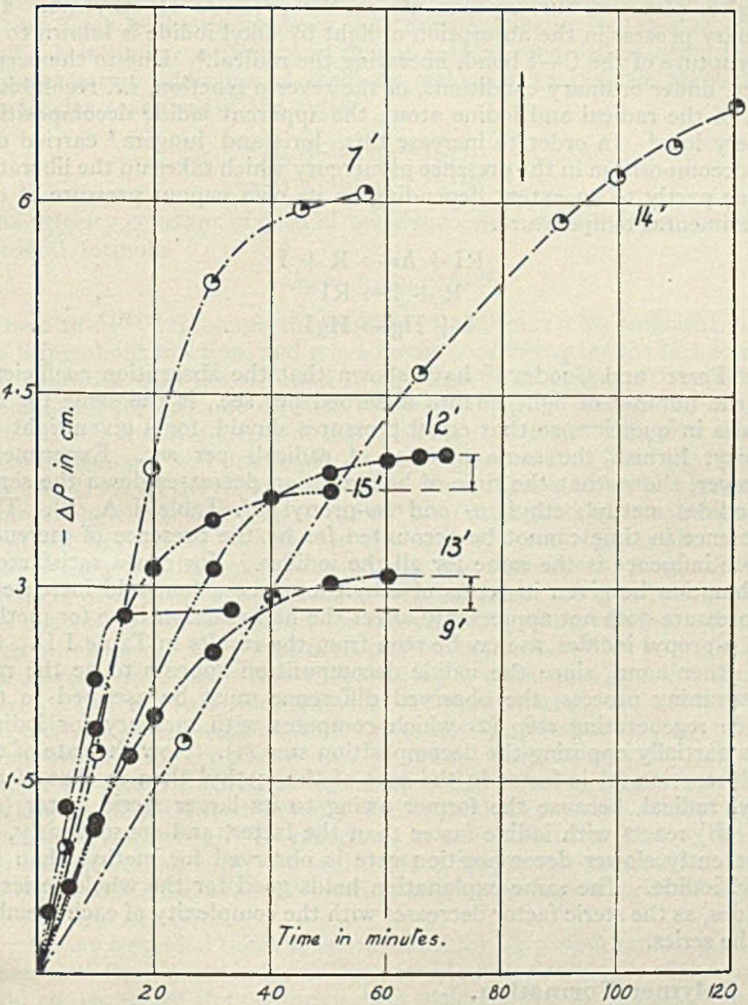

FIG. 2.—Influence of light intensity on the polymerisation yield.

## 3. General Discussion.

The discussion may be divided into three sections dealing with (*a*) the primary process of light absorption by alkyl iodides, (*b*) the formation of the polymer, (*c*) the mechanism of disappearance of radicals.

### (a) The Primary Process.

Since the photodecomposition of alkyl iodides provides the radicals necessary for the subsequent polymerisation reaction, interesting information about it may be secured by treating it separately, even though it takes place in our experiments in the presence of ethylene. The primary process in the absorption of light by alkyl iodide is known to be the rupture of the C—I bond, liberating the radical.[3] Due to the occurrence, under ordinary conditions, of the reverse reaction, *i.e.* recombination of the radical and iodine atom, the apparent iodide decomposition is very low.[4] In order to increase this, Joris and Jungers [2] carried out the decomposition in the presence of mercury which takes up the liberated iodine partly to an extent depending on its own vapour pressure at the experimental temperature.

$$\mathrm{RI} + h\nu \rightarrow \mathrm{R} + \mathrm{I} \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{R} + \mathrm{I} \rightarrow \mathrm{RI} \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathrm{I} + \mathrm{Hg} \rightarrow \mathrm{HgI} \quad . \quad . \quad . \quad . \quad (3)$$

Now Porret and Goodeve [5] have shown that the absorption coefficient, *i.e.* the number of light quanta absorbed per sec., is the same for the iodides in question, so that equal pressures should, for a given light intensity, furnish the same number of radicals per sec. Experiment, however, shows that the time of half-reaction decreases down the series of iodides methyl, ethyl, *n*- and *iso*-propyl (*cf.* Table I A, B). This difference in time cannot be accounted for by the presence of mercury, whose influence is the same for all the iodides. Nor can a satisfactory explanation be given in terms of ethylene, since a four-fold increase of its pressure does not appreciably affect the half-reaction time for methyl and *n*-propyl iodides, as may be seen from the results in Table I D. On the other hand, since the iodide decomposition appears to be the rate determining process, the observed difference must be ascribed to the iodide regenerating step (2) which competes with mercury for iodine, thus partially opposing the decomposition step (1). Now the rate of the back-reaction (2) is faster in the case of the methyl than in that of the ethyl radical, because the former owing to its larger steric factor (see sec. 3B) reacts with iodine faster than the latter, and consequently, an apparently slower decomposition rate is observed for methyl than for ethyl iodide. The same explanation holds good for the whole series of iodides, as the steric factor decreases with the complexity of each member of the series.

### (b) Polymer Formation.

In the sections 2 A and B, it was shown that with decreasing iodide pressures the polymerisation yields for the several radicals and their relative differences increased at first and then, at about 2 cm. pressure, tended to limiting values due to the progressive suppression of mutual radical combination in favour of the main ethylene polymerisation. In section 2D, the yields for methyl and *n*-propyl iodides at a pressure of

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[3] (*a*) Herzberg and Scheibe, *Z. physik. Chem.*, 1930, **7**, 390 ; (*b*) Porret and Goodeve, *Trans. Faraday Soc.*, 1937, **33**, 690.

[4] (*a*) Bates and Spence, *J. Amer. Chem. Soc.*, 1931, **53**, 1689 ; (*b*) Spence and Wild, *Proc. Leeds Phil. Soc.*, 1935, **3**, 141 ; (*c*) Iredale and Daphne Stephan, *Trans. Faraday Soc.*, 1937, **33**, 800.

[5] Porret and Goodeve, *Proc. Roy. Soc.*, 1938, **31**, 165.

2 cm. with an ethylene pressure gradually increasing up to its own limit of 25 cm. were discussed. In all these limiting cases, the yields differ for methyl and ethyl radicals by values tending to 0·5, and for methyl and *n*-propyl by unity. On the other hand, the radicals themselves differ from one another in structure by half an ethylene molecule $CH_2$. These facts lead us to believe that the polymer in the case of all the radicals is similar in form, and that it may be regarded as being formed by successive additions of ethylene molecules to radicals through bimolecular reactions of the type

$$CH_3 + C_2H_4 \rightarrow C_3H_7$$
$$C_3H_7 + C_2H_4 \rightarrow C_5H_{11} \ldots$$

the velocity constant of each of these successive steps being given by the general formula

$$k_n = p_n \cdot z_n \, e^{-E_n/RT}$$

where $ze^{-E/RT}$ represents the number of collisions with sufficient energy to bring about reaction, and $p$ is a factor accounting for the fact that not all collisions with the required energy lead to reaction. If the velocity constant $k$ for any one of these successive steps is very small, it means that that particular step will take place with extreme difficulty, and the step following it will practically not take place at all. Now the fact that the yields for all the radicals are limited to a value $n$, as we just remarked, shows ethylene is added up to the $n^{th}$ step inclusively of the above series, and not beyond it, because for the $(n + 1)^{th}$ step $k_{n+1}$ is almost zero. The reason for this may be sought in the variables $p$, $E$ and $Z$. The changes of $Z$ with each successive step are much too small compared to its absolute value to account for the vanishing value of $k_{n+1}$. If a high activation energy $E_{n+1}$ were necessary for the $(n + 1)^{th}$ step to take place an increase in temperature should bring it about and thus increase the yield. But the fact that the yield is approximately the same, despite an increase of temperature from 130 to 245° C., excludes $E$ from primary responsibility for the above state of affairs. On the contrary, the steric factor $p$, whose theoretical significance has been explained by Bawn,[6] is known to decrease markedly with complexity of the radical and to reduce correspondingly its reactivity in association reactions of the type we are concerned with. It is, therefore, the steric factor which largely affects and accounts for the limiting step of the above series of addition of ethylene to radicals.

It may be added that the steric factor for *iso*-propyl radical is smaller than that for *n*-propyl, due to the more complex structure of the former, and consequently the polymerisation yield for the *iso*-radical is slightly lower. This shows that the *n*- and *iso*-radicals when free do not lose their individuality but reveal the influence of their structural differences in polymerisation.

### (c) Disappearance of Radicals.

Regarding the disappearance of radicals, which we have several times mentioned here, three mechanisms may be envisaged, (I) saturation by capture of an hydrogen atom from a neighbouring molecule, (II) bimolecular combination of radicals among themselves, and (III) dissociation into an hydrogen atom and an olefine molecule.

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[6] Bawn, *Trans. Faraday Soc.*, 1936, **32**, 178.

$$R + XH \rightarrow RH + X \quad . \quad . \quad . \quad . \qquad I)$$
$$R + R \rightarrow RR \quad . \quad . \quad . \quad . \qquad (II)$$
$$R \rightarrow X + H \quad . \quad . \quad . \qquad (III)$$

According to mechanism (I) as established by West and his co-workers[7] for ethyl iodide decomposition, the reaction scheme will be

$$C_2H_5I \rightleftharpoons C_2H_5 + I$$
$$C_2H_5 + C_2H_5I \rightarrow C_2H_6 + C_2H_4I$$
$$. \quad . \quad . \quad .$$
$$C_2H_4I \rightarrow C_2H_4 + I$$
$$I + I + X \rightarrow I_2 + X$$

and the reaction will take place without affecting the pressure of the system. Mechanism (II) will give, as end-products, dimers of the radical and reduce the pressure, at the end of the reaction, to half its initial value.

$$2C_2H_5I \rightarrow 2C_2H_5 + I_2$$
$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$$

This mechanism, involving bimolecular combination, will become less important at low radical concentrations, or not take place at all, in which case the radicals may disappear through mechanism (I). In favour of both these mechanisms we cite the work of Joris and Jungers[2] who found that the photodecomposition of ethyl iodide in presence of mercury (when the radical concentration was high), took place with a pressure variation, and in the absence of mercury, without pressure variation. A similar observation was made by Van Tassel,[8] also in this laboratory, studying the same reaction thermally. It is no doubt to the exclusive occurrence of mechanism (I) that the end-products, ethane and ethylene obtained by West and Ginsburg[7] in ethyl iodide decomposition, and propane and propylene by Glass and Hinshelwood,[9] and Jones and Ogg[10] in propyl iodide decomposition, are to be attributed. In the mercury photosensitised hydrogenation of ethylene, where radical combination must have been appreciable, Jungers and Taylor[11] got almost exclusively butane due to the occurrence of mechanism (II).

Our results do not confirm mechanism (III), *i.e.* dissociation of the radical into an atom of hydrogen and olefine, which has been frequently suggested by several authors, since we do not find even traces of hydrogen in the reaction products.

Consequently, we suggest that in our case mechanism (I) and (II) are both responsible for the disappearance of radicals, the former at low, the latter at high, and both together at intermediate radical concentrations. Further experiments are in progress to analyse completely the products of decomposition of, and the products resulting from the polymerisation induced by alkyl iodides containing upwards of five carbon atoms, in order to throw more light on the proposed mechanisms.

The authors wish to express their thanks to Professor H. S. Taylor of Princeton University for opportunity afforded to discuss certain problems raised in this paper.

[7] West and Ginsburg, *J. Amer. Chem. Soc.*, 1934, **56**, 2626 ; West and Schlessinger, *J. Amer. Chem. Soc.*, 1938, **60**, 961.

[8] Van Tassel, *Natuurwet, Tydschrift*, 1938, **20**, 83.

[9] Glass and Hinshelwood, *J. Chem. Soc.*, 1929, 1817.

[10] Jones and Ogg, *J. Amer. Chem. Soc.*, 1937, **59**, 1931.

[11] Jungers and Taylor, *J. Chem. Physics*, 1938, **6**, 325.

## Summary.

1. The polymerisation of ethylene by alkyl radicals has been examined. The yield for any one radical increases with increasing ethylene pressure, decreasing iodide pressure and light intensity. For the radicals taken together, it decreases down the series methyl, ethyl, *n*- and *iso*-propyl.

2. The polymer is formed by bimolecular additions of ethylene molecules to radicals. The differences in the photodecomposition rates of the alkyl iodides and their polymerisation yield differences are explained in terms of steric factor.

3. The structural differences between *n*- and *iso*-propyl iodides are clearly revealed both in their photodecomposition rates and polymerisation yields.

4. Two mechanisms account for the disappearance of radicals in this polymerisation, *i.e.* saturation through capture of an hydrogen atom and bimolecular recombination of radicals.

*Laboratorium voor Physische Scheikunde*
*der Universiteit te Leuven* (*Louvain*),
*Belgium.*

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# THE SURFACE TENSIONS OF METHYL ACETATE SOLUTIONS.

By J. W. Belton.

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There appear to be no accurate data available for the surface tensions of aqueous solutions of methyl acetate—those quoted in the International Critical Tables, for example, are only given to within 2 % Measurements were therefore made on mixtures of water and redistilled methyl acetate by the maximum bubble pressure method, but using the procedure previously described by the writer,[1] it was found impossible to obtain reproducible results, although no difficulty had been experienced with other organic liquids.[2] By taking suitable precautions, however, it was finally found possible to obtain values with a maximum error of 0·3 %.

The experimental cell was modified by sealing into the side wall (Fig. 1, ref. [1]), a piece of platinum wire bent at right angles and sharpened so that its point was about 0·5 cm. above the jet. The surface of the liquid under observation was altered by a finely adjustable pressure head so that it was coincident with the platinum point when observed with the cathetometer telescope. The measured maximum bubble pressure must be corrected by the head of liquid between the jet and the point; this correction involves the density of the solution and the (directly measured) distance between jet and point, also given by measurements of the maximum bubble pressure for water with its surface at the jet and then with its surface at the point (the position of the jet relative to the point was constant for all determinations).

Some difficulty was experienced in obtaining a uniform, slow rate of bubbles (about 1 per 10 sec.). The pressure tended to mount to a value greater than that for the maximum bubble pressure and then to be released

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[1] Belton, *Trans. Faraday Soc.*, 1935, 31, 1413.

[2] *Ibid.*, 1642.

in a burst of five or six bubbles. By careful adjustment of the pressure, however, a uniform rate was obtained, but only below the maximum concentration recorded below; above this value the bubbles appeared in batches at irregular intervals, with consequent oscillation in the manometer and irreproducibility of results.

Attempts were made to measure the surface tensions by the capillary rise method. The jet was replaced by a capillary tube; the liquid was kept at a fixed level by means of the platinum point, and the pressure necessary to depress the meniscus inside to that outside was measured with the aid of the cathetometer telescope. The results agreed with the bubble pressure method, but for the more concentrated solutions which had given previous trouble, it was not found possible to keep the levels inside and out the same. The failure of the two methods for the stronger solutions is probably linked with the high volatility of methyl acetate.

The methyl acetate used in these experiments had been carefully purified by the method of Young and Thomas,[3] allowed to stand repeatedly over phosphorus pentoxide (which removes both water and alcohol) and distilled. Its density at 25° C. was 0·9296 g./c.c. The water used was distilled from quartz and was stored in a quartz vessel. All measurements were made at 25° C.

## Methyl Acetate-Water Mixtures.

TABLE I.

| $N_{\mathrm{MeAc.}}$ | $h$. | $\gamma$. |
|---|---|---|
| | | 72·01 |
| 0·00161 | 13·525 | 66·33 |
| 0·00321 | 12·83 | 62·92 |
| 0·00567 | 11·87 | 58·22 |
| 0·00904 | 11·235 | 55·08 |

The measured surface tensions are given in Table I, in which $h$ is the maximum bubble pressure in cms. of butyl phthalate and the concentrations are expressed as mole fractions of methyl acetate. The plot of $\gamma - N_{\mathrm{MeAc}}$ gives a smooth curve which becomes less steep as the concentration of methyl acetate increases. The vapour pressures of methyl acetate solutions have been determined by McKeown and Stowell,[4] and the plot of their data shows that over the concentration range investigated here Henry's law is obeyed. Assuming that the surface excess of water is zero, that of methyl acetate may then be calculated from

$$d\gamma = -\Gamma_{\mathrm{MeAc}} RT \, d \ln N_{\mathrm{MeAc}}. \quad . \quad . \quad . \quad (1)$$

These are given in moles/sq. cm. for rounded concentrations in Table II.

TABLE II.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $N_{\mathrm{MeAc}}$ . | 0·001 | 0·002 | 0·003 | 0·004 | 0·005 | 0·006 | 0·0075 |
| $\Gamma \times 10^{10}$ . | 0·58 | 0·81 | 1·16 | 1·41 | 1·58 | 1·27 | 1·25 |

The maximum surface excess which occurs at a concentration of methyl acetate of $N_{\mathrm{MeAc}} = 0{\cdot}005$ corresponds to an area per molecule of 105 A². The value of $\Gamma$ calculated here is that according to the convention of Gibbs, but for low concentrations it is approximately the same as that based on a comparison of equal volumes of liquid.[5] The area per molecule calculated for the total number of molecules in the

[3] Young and Thomas, *J. Chem. Soc.*, 1893, **63**, 1191.

[4] McKeown and Stowell, *ibid.*, 1907, 97.

[5] Guggenheim and Adam, *Proc. Roy. Soc.*, *A*, 1933, **139**, 227.

surface is then 79 A$^2$; and the corresponding figure for a concentration of methyl acetate of $N_{\mathrm{MeAc}} = 0{\cdot}001$ is 220 A$^2$. The area per molecule for insoluble long chain esters is given by Adam as 22 A$^2$. There is thus ample space for the methyl acetate to be accommodated in the surface layer.

## Methyl Acetate-Water-Sucrose Mixtures.

The influence of sucrose on the adsorption of methyl acetate is of interest. The surface tensions of a series of methyl acetate-water-sucrose mixtures in which the methyl acetate content was kept constant while water and sucrose were added in equimolar quantities, were measured by the method described above. The surface tension increased with sucrose concentration and decreased with that of methyl acetate. This is similar to the effect of both these substances on pure water. The results are given in Table III, which gives the number of moles of methyl acetate, the mole fraction of each component, the maximum bubble pressure, the surface tension and the surface excesses of methyl acetate ($\Gamma_1$) and of water ($\Gamma_3$).

These surface excesses were calculated from the Gibbs equation, in which it has been assumed that the activities of the components may be replaced by their mole fractions. This procedure is partly justified by the data of McKeown and Stowell;[4] the partial pressure of methyl acetate is proportional to its mole fraction and that of water nearly proportional over the concentration range investigated here. We have then

$$d\gamma = -\Gamma_1 RT \, d \ln N_1 - \Gamma_3 RT \, d \ln N_3 \quad . \quad . \quad (2)$$

TABLE III.

| $N_1$. | $N_2$. | $N_3$. | $h$. | $\gamma$. | $\Gamma_1 \times 10^{10}$. | $\Gamma_3 \times 10^{10}$. |
|---|---|---|---|---|---|---|
| **$m_1 = 0{\cdot}00446$.** | | | | | | |
| 0·001604 | 0·004962 | 0·9935 | 13·59 | 66·65 | 1·9 | 28·6 |
| 0·001590 | 0·009800 | 0·9890 | 13·69 | 67·14 | | |
| 0·001574 | 0·01455 | 0·9840 | 13·78 | 67·60 | | |
| 0·001559 | 0·01922 | 0·9793 | 13·87 | 68·05 | | |
| 0·001544 | 0·02379 | 0·9745 | 13·905 | 68·20 | | |
| **$m_1 = 0{\cdot}00892$.** | | | | | | |
| 0·003223 | 0·004984 | 0·9915 | 12·895 | 63·25 | 2·6 | 20·3 |
| 0·003193 | 0·009842 | 0·9870 | 12·99 | 63·75 | | |
| 0·003161 | 0·01462 | 0·9823 | 13·03 | 63·90 | | |
| 0·003132 | 0·01931 | 0·9777 | 13·07 | 64·09 | | |
| 0·003095 | 0·02385 | 0·9730 | 13·165 | 64·57 | | |
| **$m_1 = 0{\cdot}01581$.** | | | | | | |
| 0·005758 | 0·005023 | 0·9890 | 11·94 | 58·56 | 4·3 | 16·8 |
| 0·005705 | 0·009917 | 0·9845 | 12·015 | 58·92 | | |
| 0·005646 | 0·01472 | 0·9795 | 12·055 | 59·13 | | |
| 0·005594 | 0·01945 | 0·9750 | 12·145 | 59·55 | | |
| 0·005539 | 0·02407 | 0·9703 | 12·27 | 60·17 | | |

where $N_1$ and $N_3$ are the mole fractions of methyl acetate and water respectively; the surface excess of sucrose has been put equal to zero. This expression may be differentiated with respect to $m_1$ and $m_2$, the number of moles of methyl acetate and sucrose present, and we obtain

$$-\frac{1}{RT}\left(\frac{\partial \gamma}{\partial m_1}\right)_{m_2} = -(\Gamma_1+\Gamma_3)\left(\frac{\partial \ln N}{\partial m_1}\right)_{m_2} + \frac{\Gamma_1}{m_1} + \Gamma_3\left(\frac{\partial \ln m_3}{\partial m_1}\right)_{m_2} \qquad (3)$$

and

$$-\frac{1}{RT}\left(\frac{\partial \gamma}{\partial m_2}\right)_{m_1} = -(\Gamma_1+\Gamma_3)\left(\frac{\partial \ln N}{\partial m_2}\right)_{m_1} + \Gamma_3\left(\frac{\partial \ln m_3}{\partial m_2}\right)_{m_1} \qquad (4)$$

where $N$ is the total number of moles present, which has been taken as constant for a series, although it does vary, but by no more than 2 %. All the slopes involved may be calculated from the data, and the values of $\Gamma_1$ and of $\Gamma_2$ evaluated.

Both methyl acetate and water are positively adsorbed at the surface in constant amounts for each series (actually $\Gamma_1$ shows a decrease and $\Gamma_3$ an increase of about 2 % in each series with increasing sucrose content). The effect of sucrose is to increase the amount of methyl acetate in the surface, but the extent of the increase is independent of the amount of sucrose present. The amount of water adsorbed is also constant, and is approximately independent of the amount of sucrose, although for aqueous sucrose solutions the adsorption of water varies from about 29 to 17 $10^{-10}$ moles/sq. cm. for the same range of sucrose concentration. As the methyl acetate adsorption increases with increasing methyl acetate content, that of water is reduced, which suggests that water is pushed out of the surface layer and methyl acetate comes in to take its place.

## Summary.

The surface tensions of aqueous methyl acetate solutions have been measured to within 0·3 %, and the surface adsorptions calculated. The effect of the addition of sucrose has been investigated, and it is found that the amount of methyl acetate in the surface is increased, but that the increase is independent of the amount of sucrose added ; the amount of water adsorbed is also shown to be independent of the amount of sucrose.

*Physical Chemistry Department,*
*The University,*
*Leeds*, 2.

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# MONOLAYERS OF A LONG CHAIN ESTER SULPHATE.

By Einar Stenhagen.*

*Received* 17*th January*, 1940.

The strong water affinity of the —O—$SO_3'$ group makes it necessary to attach a very long hydrocarbon chain to it in order to obtain an insoluble monolayer on water. With a chain containing 22 carbon atoms insoluble monolayers, presenting some interesting features, are obtained.

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* Rockefeller Foundation Fellow, 1938-39.

## Experimental.

The measurements were carried out using a Langmuir-Adam trough and a polonium electrode in the usual manner.[1] The potentials were measured with a Lindemann electrometer.

The spreading of the sodium docosyl sulphate presented some difficulty as the sulphate does not dissolve in non-polar organic solvents. Ethyl alcohol was therefore used as solvent, but as this is completely water miscible and the sulphate group is very hydrophilic, 20-50 % of the material spread is lost into the substrate. On leaving the film under no pressure for two hours about 95 % of the amount spread is found in the surface. Once a monolayer is formed, it is very stable and shows no detectable tendency to dissolve.

## Properties of $C_{22}$ Ester Sulphate Monolayers.

Fig. 1 shows the results obtained with the sulphate spread on M/25 phosphate buffer (Clark and Lubs), *p*H 7·2 and 0·01 N. HCl respectively. Due to the loss of material during the process of spreading the force-area curves in Fig. 1 have been plotted assuming that the area of the molecule just before collapse at about 65 dynes pressure is 18·5 A.[2] This is the smallest possible area to which a hydrocarbon chain in a monolayer can be compressed before the monolayer collapses (compare Dervichian [2]) and it is reasonable to assume that the area of the $C_{22}$ ester sulphate at the collapse point has reached this value. The projections of the very slightly compressible high pressure region *b-c* on both F-A curves in Fig. 1 cut the axis at an area of about 20·5 A.[2] which is the same as the mean value, 20·5 A.[2], found by Adam [3]

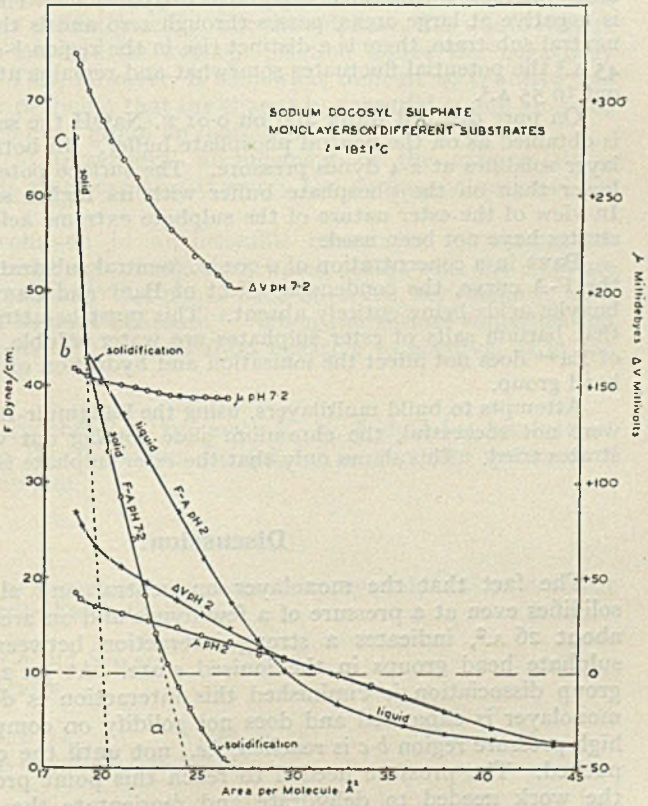

FIG. 1.

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

[2] D. G. Dervichian, *Thèses*, Paris 1936, Masson et Cie.

[3] N. K. Adam, *The physics and chemistry of surfaces*, 2nd edition, Oxford, 1938, p. 48.

for a large number of long chain compounds. At *p*H 7·2, the projection of the straight part of the F-A curve between 13 and 43 dynes cuts the axis at about 24·5 A.$^2$. This area (Adam's "area of zero compression" [3] is 24 A.$^2$ for the $C_{22}$ fatty acid on 0·01 N. HCl and the F-A curve for the $C_{22}$ sulphate on phosphate substrate at neutral *p*H therefore resembles the curves obtained with carboxylic acids in the undissociated form. The pressure values are considerably higher, however, and it is necessary to apply more than 40 dynes pressure before the incompressible region *b-c* is reached (about 24 dynes in case of carboxylic acids). The monolayer is extremely stable and can be left for several minutes at 60 dynes without appreciable fall in pressure. The monolayer is already solid at a pressure of 3 dynes at an area of 26 A.$^2$. The surface potential $\Delta V$ and the corresponding surface moment $\mu$ are low. The potential is uniform to 4 millivolts and $\mu$ is nearly constant at about 150 millidebyes, slowly rising on compression of the monolayer. There is a distinct small rise in the high pressure region above 40 dynes.

On 0·01 N. hydrochloric acid (Fig. 1, *p*H 2) the monolayers are expanded. On compression solidification of the monolayer does not occur until the incompressible region is reached above 40 dynes/cm. The surface potential is negative at large areas, passes through zero and is then rising. As on neutral substrate, there is a distinct rise in the region *b-c* (Fig. 1). Above 45 A.$^2$ the potential fluctuates somewhat and remains at about − 40 mV. out to 55 A.$^2$.

On pure distilled water and on 0·01 N. NaOH the same type of curve is obtained as on the neutral phosphate buffer. In both cases the monolayer solidifies at 2-4 dynes pressure. The surface potential is somewhat lower than on the phosphate buffer with its higher salt concentration. In view of the ester nature of the sulphate extreme acid or alkaline substrates have not been used.

$Ba^{++}$ in a concentration of 0·001 N. (neutral substrate) does not affect the F-A curve, the condensing effect of $Ba^{++}$ and $Ca^{++}$ found for carboxylic acids being entirely absent. This must be attributed to the fact that barium salts of ester sulphates are water soluble, *i.e.*, the presence of $Ba^{++}$ does not affect the ionisation and hydration of the ester sulphate head group.

Attempts to build multilayers, using the Langmuir-Blodgett technique, were not successful, the chromium slide coming out wet from all substrates tried. This shows only that the ester sulphate is very hydrophilic.

## Discussion.

The fact that the monolayer on neutral and alkaline substrates solidifies even at a pressure of a few dynes and an area per molecule of about 26 A.$^2$, indicates a strong interaction between the (hydrated) sulphate head groups in the ionised state. At *p*H 2, when the head group dissociation is diminished this interaction is decreased and the monolayer is expanded and does not solidify on compression until the high pressure region *b-c* is reached, *i.e.*, not until the chains are closely packed. The pressure needed to reach this point probably represents the work needed to dehydrate and reorientate the head group. In general, monolayers are expanded or gaseous when the head groups are fully dissociated, as shown by carboxylic acids on very alkaline solutions [4] and primary amines on acid solutions. In the case of the former the partly dissociated state in the neutral *p*H range makes the monolayers condensed, due to ion-dipole interaction. The behaviour

[4] N. K. Adam and J. Miller, *Proc. Roy. Soc.*, *A*, 1933, **142**, 401.

of the sulphate is contrary to this general behaviour as the ionised monolayer is solid at a few dynes pressure and an area of 26 A.$^2$.

Very long hydrocarbon chains tend to make the films solid, but the nature of the head group is still more important, for instance, pyridinium bromide, with a 22 carbon chain forms gaseous films.[5] Long chain ureas [6] below a certain temperature are solid at 26 A. The urea differs from the sulphate in that the monolayer is extremely incompressible whereas the latter can be compressed to the area occupied by the closely packed chain.

The vertical component of the dipole moment of the complicated head group decreases on decreasing ionisation, which can be compared with that of fatty acids which increases under the same condition and that of primary amines, which is fairly constant irrespective of the degree of ionisation.

In the case of carboxylic acids, the decrease in $\mu$ is attributed [7] to the introduction of an additional dipole on ionisation, consisting of the positive ion below and the negative oxygen above, which neutralises the dipole present in the fatty acid. For the sulphate, this would require that the positive ion had an average position above the negatively charged oxygen. This, however, is somewhat difficult to conceive and it is perhaps more probable that the change in potential is due to some reorientation of the head group on ionisation.

The symmetrical tetrahedral arrangement of the oxygen atoms around the sulphur atom explains the very low surface potential of the unionised sulphate.

It is very uncommon in an insoluble monolayer for the surface potential to change sign on compression, which occurs with the sulphate on 0·01 N. HCl substrate; but it has been observed, for instance, with adsorbed layers of sodium benzoate.[8] When the surface concentration is increased, the potential changes from negative to positive, as in the case of the sulphate.

The author is indebted to Professor E. K. Rideal for his interest and advice, and to Dr. T. Malkin, Bristol, for a very pure specimen of sodium docosyl sulphate.

## Summary.

The properties of monolayers of sodium docosyl sulphate on different substrates are described and discussed.

*Department of Colloid Science,*
*Cambridge.*

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[5] Adam, *l.c.* [3], p. 129. [6] *Ibid.*, p. 55. [7] *Ibid.*, p. 72.

[8] Frumkin, *cf.* Adam, *l.c.* [3], p. 136.

# THE CONVERSION OF PARAHYDROGEN BY PORPHYRIN COMPOUNDS, INCLUDING HEMOGLOBIN.

By D. D. Eley.

*Received 9th January*, 1940.

The conversion of *para*hydrogen by paramagnetic gases, and by paramagnetic gases and ions in solution, was discovered by Farkas and Sachsse.[1, 2] A theoretical treatment by Wigner[3] showed that under the influence of an inhomogeneous magnetic field a parahydrogen molecule exhibits an observable probability for the para-ortho transition, the calculated collision efficiency of $10^{-12}$ to $10^{-14}$ agreeing with experiment. Such a mechanism is also considered to account for the conversion at low temperatures on many heterogeneous catalysts, such as charcoal,[4, 5] and metals, metallic oxides and salts.[6] The conversion on those catalysts which are diamagnetic is attributed to a surface paramagnetism. We have examined a number of compounds of the porphyrin type, both as heterogeneous catalysts and in solution, which might be expected to be free from such complications, and find that the paramagnetic compounds show a conversion of the kind discussed. The absence of any true activation of hydrogen is not unexpected, since in biochemical systems the heme compounds appear to be usually associated with an activation of oxygen through the ferric-ferrous change.[7] Some experiments on the closely related structures, metal-free phthalocyanine and copper phthalocyanine, are included.

## Experimental.

All experiments were made under static conditions. The heterogeneous catalysts were examined in glass vessels of 150 c.c., which could be evacuated to $10^{-6}$ mm., and which were connected to a system consisting of manometers, storage bulbs for the gases used, and the thermoconductivity apparatus. The solutions were placed in a 100 c.c. vessel, which was attached to the apparatus by a flexible glass spiral tube, so that it could be shaken at 4 to 5 vibrations per second. The *para* $H_2$ and total D-content analyses were made, on small samples withdrawn from the reaction vessel by the method of Farkas,[8] and the $H_2 + D_2 = 2HD$ analyses by the method of Melville and Bolland.[9]

The blood corpuscles, obtained by centrifuging ox-blood, were washed with Ringer's solution, and suspended in this solution for an experiment. The hematin was the brown amorphous powder supplied by B. D. H. The hemin consisted of well-formed crystals prepared according to Gattermann's *Laboratory Methods of Organic Chemistry*, 1932, page 395.

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[1] Farkas and Sachsse, *Z. physikal. Chemie B*, 1933, **23**, 1.

[2] *Ibid.*, 19.

[3] Wigner, *ibid.*, 28.

[4] Bonhoeffer, Farkas and Rummel, *ibid.*, **21**, 225.

[5] Rummel, *ibid.*, **167**, 221.

[6] Taylor and Diamond, *J. Amer. Chem. Soc.*, 1935, **57**, 125.

[7] Warburg, *Biochem. Z.*, 1924, **152**, 479.

[8] Farkas, *Z. physikal. Chemie B*, 1933, **22**, 344; Eley and Tuck, *Trans. Faraday Soc.*, 1936, **32**, 1425.

[9] Melville and Bolland, *ibid.*, 1937, **33**, 1316.

The hematoporphyrin was obtained from Dr. Theodore Schuchardt. The metal-free phthalocyanine and copper phthalocyanine were kindly supplied by Professor R. P. Linstead ; a second sample of copper phthalocyanine was prepared by twice extracting with quinoline a sample of I.C.I. " Monastral fast blue " powder, previously baked out *in vacuo* for 30 hours at 300° C. The hydrogens were purified by palladium.

## Heterogeneous Conversion.

In this paper conversions are expressed by the constant $k=1/t \ln C_0/C_t$, where $C_0$ is the effective concentration of parahydrogen at the beginning of the experiment (*i.e.* excess over the equilibrium value) and $C_t$ is the effective concentration at time $t$. In agreement with earlier work, this equation was found applicable for all the heterogeneous and dissolved catalysts examined. Care was taken to outgas all catalysts at temperatures well below those at which decomposition starts. Table I. shows that at room temperature and lower temperatures a conversion is catalysed by the paramagnetic solids, but not by the diamagnetic solids. It also shows an absence of any $H_2 + D_2$ reaction, in the case of the heme compounds at the maximum working temperature. These

TABLE I.

| Catalyst. | $\mu$, Bohr Magnetons. | $T$° C. | $p$ mm. | $t$ Hours. | $k$ Hours$^{-1}$. |
|---|---|---|---|---|---|
| Hematoporphyrin | 0·0[a] | | | | |
| 100 mg. | | 22 | 14 $pH_2$ | 24 | — |
| 200 mg. | | 100 | 100 $H_2D_2$ | 288 | — |
| Hematin | 5·6[b] | 20 | 65 $pH_2$ | 17·3 | 0·036 |
| 200 mg. | | 20 | 6 $pH_2$ | 3·1 | 0·039 |
| | | | | 6·0 | 0·036 |
| | | | | 9·0 | 0·036 |
| | | | | 22·0 | 0·035 |
| | | 20 | 0·8 | 3·1 | 0·038 |
| 400 mg. | | 20 | 16 $pH_2$ | 23·8 | 0·075 |
| | | 100 | 40 $H_2D_2$ | 480 | — |
| Hemin 100 mg. | 5·8[b] | 185 | 20 $pH_2$ | — | 0·012 |
| | | 20 | 20 $pH_2$ | — | 0·011 |
| 700 mg. | | 120 | 40 $H_2D_2$ | 288 | — |
| | | 121 | 33 $pH_2$ | 17·7 | 0·066 |
| | | −80 | 30 $pH_2$ | 3·5 | 0·063 |
| Metal-free Phthalocyanine | | | | | |
| 150 mg. | 0·0[c] | −80 | 27 $pH_2$ | 63 | — |
| Copper Phthalocyanine | | | | | |
| 390 mg. | 1·7[d] | −80 | 21 $pH_2$ | 16·2 | 0·004 |
| 400 mg. | | −80 | 40 $pH_2$ | — | 0·003 |
| | | 20 | 40 $pH_2$ | — | 0·001 |
| 4·4 g. (from Monastral blue) | | 20 | 30 $H_2D_2$ | 144 | — |
| | | −80 | 28 $pH_2$ | 3·2 | 0·186 |
| | | 0 | 26 | 16·9 | 0·082 |
| | | 20 | 23 | 24·0 | 0·021 |
| | | 20 | 23 | 23·0 | 0·023 |
| | | 112 | 27 | 16·5 | 0·014 |

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[a] Inferred from measurements on related porphyrins, by Haurowitz and Kittel, *Ber.*, 1933, **66**, 1046.

[b] Pauling and Coryell, *Proc. Nat. Acad. Sci.*, 1936, **22**, 159.

[c] Lonsdale, *J.C.S.*, 1938, 364.

[d] Klemm and Klemm, *J. prak. Chemie*, 1935, **143**, 82.

data establish the conversions as of the paramagnetic type. At 200°–300° C. an $H_2 + D_2$ reaction has been observed on a number of phthalocyanines, but since this property would appear to involve some activation of the catalyst,[10] we are not concerned with it here.

In Table I. and Fig. 1 we give some data on the kinetics, showing the applicability of $k$ and its independence of pressure. For hematin and copper phthalocyanine the temperature coefficients are negative, corresponding respectively to apparent activation energies of — 1300 and about — 2300 cals. This behaviour is similar to that previously observed, and from the published constants at two temperatures for charcoal, Ni, Cu and NaCl in the low temperature region we estimate apparent activation energies of — 400 to — 1600 cal. Bonhoeffer, Farkas and Rummel consider that on charcoal the reaction of the $H_2$ molecules in the adsorbed layer proceeds with zero true activation energy, and the apparent activation energy is to be associated with the heat of Van der Waal's adsorption of $H_2$ on the catalysts. That such is not necessarily the case is shown by the data for hemin, where $k$ is independent of temperature over — 80° C. to 180° C.; the absence of any $H_2 + D_2$ reaction rules out the possibility that the catalyst is in the intermediate range between low and high temperature mechanisms such as was observed for charcoal. Such an independence of temperature would be observed if every molecule during its stay in the adsorption layer were converted, when the reaction velocity would be given by the number desorbing per second. If we approximate the adsorbed layer as a two-dimensional gas, then the desorption velocity is equal to the classical number of collisions with the surface.[11] From a microscopic measurement of the average size of crystal, we roughly attribute to the hemin a surface of 100 cm.$^2$ per 100 mg. Such a quantity of hemin converts $3{\cdot}0 \times 10^{14}$ molecules of *para* $H_2$ per second at 20° C. and 20 mm. pressure. Since the collision number is $2{\cdot}9 \times 10^{24}$ molecules sec.$^{-1}$, it is clear that desorption is not the rate-determining step, and in fact the collision yield of $10^{-10}$ is similar in order to that found for gaseous $O_2$ as catalyst, where it is about $10^{-12}$.[1] We are inclined to attribute the behaviour of hemin to the fact that an actual activation energy is

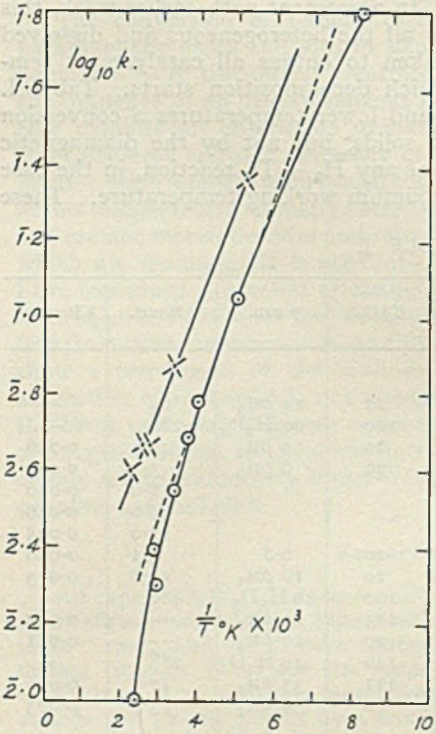

FIG. 1.—Parahydrogen conversion on Solid Hematin. (X 0·04g. specimen. O 0·02g. specimen.)

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[10] Polanyi, *Trans. Faraday Soc.*, 1938, 34, 1191.

[11] Kimball, *J. Chem. Physics*, 1938, 6, 447.

required for reaction in the adsorption layer, in magnitude fortuitiously equal to the energy of adsorption. Such an energy might well be required to bring the $H_2$ molecule sufficiently close to the magnetic centre for the ordinary transition probability to be reached. A similar activation might be expected for the paramagnetic ions, where a partial penetration of the hydration shell is considered necessary.[12, 13] The temperature coefficients of these reactions have not been measured, however. The structures of hemin and hematin being so analogous, it is difficult to see *a priori* why they should show this difference in behaviour, which might indeed be a function of the mode of preparation (only one hemin preparation was examined). Even if this is so, the significance of the observation stands, and a detailed investigation of the temperature coefficients of conversion and of the adsorption will be necessary to clear up the matter.

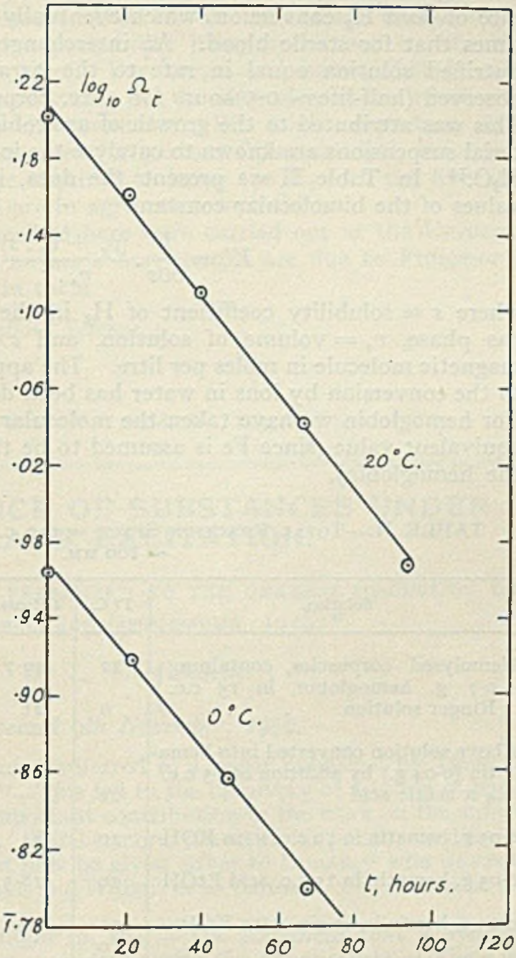

FIG. 2.—Parahydrogen conversion by 0·05 g. Hemin in 10 c.c. N/10 KOH. ($\Omega$ is the resistance value of the $pH_2$, and is proportional to $C_t$.)

## Conversion in Solution.

Hemoglobin, hemin and hematin solutions were examined. A sterile solution of blood corpuscles showed no interchange on being shaken for 20 hours with $D_2$ gas; we can therefore conclude that the dehydrogenases present in blood will not catalyse the interchange between $D_2$ and water. The *para* $H_2$ reaction observed was attributed to the hemoglobin, which is the main paramagnetic substance present in the corpuscles. Hemolysis of the corpuscles, by freezing and thawing, produced no appreciable alteration in *k*. In the absence of a small

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[12] Sachsse, *Z. physikal. Chemie B*, 1934, 24, 429.

[13] Sachsse, *Z. Electrochemie*, 1934, 40, 531.

addition of boric acid or thymol, putrefaction set in after 2-3 days' shaking in hydrogen. This was accompanied by a rapid increase in the rate of *para* $H_2$ conversion, which eventually reached a value 10 to 40 times that for sterile blood. An interchange between $D_2$ gas and the putrified solution equal in rate to the *para* $H_2$ conversion was also observed (half-life $\sim$ 0·5 hours for 4 c.c. corpuscles in 10 c.c. solution). This was attributed to the growth of anærobic bacteria, as certain bacterial suspensions are known to catalyse the interchange between $D_2$ and $H_2O$.[14] In Table II we present the data, in the last column giving values of the bimolecular constant

$$K' = \frac{k}{60s} \cdot \frac{(v_g + v_s \,.\, s)}{v_s \,.\, c},$$

where $s$ = solubility coefficient of $H_2$ in the solvent, $v_g$ = volume of gas phase, $v_s$ = volume of solution, and $c$ = concentration of paramagnetic molecule in moles per litre. The application of such a formula to the conversion by ions in water has been demonstrated by Sachsse.[12] For hemoglobin we have taken the molecular weight as 17,000, the Fe-equivalent value (since Fe is assumed to be the paramagnetic centre of the hemoglobin).

TABLE II.—TOTAL REACTION SPACE = 110 C.C., HYDROGEN PRESSURE $\sim$ 100 MM.

| Solution. | $T$° C. | $t$ Hours. | $k$ Hours$^{-1}$. | $K'$ mol.$^{-1}$ l. min$^{-1}$. |
|---|---|---|---|---|
| Hemolysed corpuscles, containing 0·7 g. hemoglobin, in 15 c.c. Ringer solution | 22 | 19·7 | 0·023 | 49·6 |
| | 0 | 21 | 0·023 | 42·5 |
| Above solution converted into hematin (0·04 g.) by addition of 15 c.c. 4 N acetic acid | 22 | — | 0·0042 | 4·7 |
| 0·05 g. hematin in 10 c.c. N/10 KOH | 20 | 44 | 0·004 | 4·4 |
| 0·03 g. hematin in 15 c.c. acid EtOH | 20 | 18·5 | 0·007 | 2·7 |
| 0·05 g. hemin in 10 c.c. N/10 KOH | 20 | — | 0·0058 | 6·4 |
| | 0 | — | 0·0055 | 5·2 |

Values of $s$, $H_2/H_2O$ 0° C. = 0·021
,, 20° C. = 0·018
$H_2/C_2H_5OH$ 20° C. = 0·086.
(Landolt-Bornstein)

Our values of $k$ for hemin and hematin agree well with those found for $O_2$ in $H_2O$ of 10·5,[1] and for $Fe^{+++}$ in $H_2O$ of 7·5.[13] On the simple assumption of identical transition probabilities, this means that there is no appreciable steric factor for the reaction with hematin. Since the porphyrin molecule is approximately flat and contains the active centre, $Fe^{+++}$, in the middle of the structure, we might expect the number of collisions between $Fe^{+++}$ and the small $H_2$ molecule to be not very restricted below the value for the free ion in water. The value of $k$ for hemoglobin is significantly larger than that for hemin and hematin. Since hemoglobin is pictured as a spherical molecule of molecular weight

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[14] Cavanagh, Horiuti and Polanyi, *Nature*, 1934, 133, 797.

64,000, with the four hemes on the surface,[15] the ordinary classical collision number can only be approximately valid. The reaction rate is probably assisted by adsorption of $H_2$ on the surface of the colloid particle, a rise in reaction probability being occasioned by the time spent in the adsorption layer. For hemin and hemoglobin $k$ is but little influenced by temperature, but a discussion must await more accurate and extensive measurements. We might expect a rather larger effect than was observed for gaseous $O_2$ as catalyst, because an activation energy will be required to bring the $H_2$ into the hydration layer ; the results listed are in agreement with this.

The experiments described here were carried out at the University of Manchester, and the author's best thanks are due to Professor M. Polanyi for his interest in them.

*The Department of Colloid Science,*
*The University,*
*Cambridge.*

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[15] Pauling, *Proc. Nat. Acad. Sci.*, 1935, 21, 186.

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# LUMINESCENCE OF SUBSTANCES UNDER FLAME EXCITATION.

## ADDENDUM TO PAPER PRESENTED TO THE GENERAL DISCUSSION ON LUMINESCENCE (SEPTEMBER, 1938).*

By L. T. Minchin.

*Received 9th November*, 1939.

On page 171 Thomaschek referred to a paper published by Tiede and H. Thomaschek in 1925.[43] This led to the discovery of a group of papers which represent a very important contribution to the work on the subject, and are here summarised. Furthermore, the claim for priority in discovering the phenomenon must now be given either to Donau,[40] who described it seven years before Nichols and Wilbur, or to Balmain, who described it in 1842.[44]

**Conditions of Experiment** (p. 164).—The statement that a hydrogen flame is essential is not in accordance with the experiments of Tiede and Buscher,[41] who found BN excited to luminescence by flames of

$$H_2, C_2H_5OH, H_2S, CS_2$$

and other substances ; also by the flame of $Cl_2$ burning in excess $H_2$. If a " flame-separator " is employed, the edge of the inner cone is found somewhat more effective in producing luminescence than the outer mantle of the $H_2$-in-air flame.

The luminescence can be observed on a bead in a loop of platinum wire by passing it slowly through the flame. Under these conditions the luminescence of CaO + trace Bi (cyanide blue colour) and of CaO + trace Mn (deep yellow) has been observed by the author (L. T. M.).

**Substances showing Luminescence** (p. 165).—To these must be added elements from the odd series of Group 5, Sb, and Bi especially, as activators in CaO, and also Mn under the same conditions. Boron nitride is also luminescent when crystalline, a condition usually associated with the presence of boric acid. X-ray spectra show that the phenomenon depends on the boron nitride being crystalline.[39] It is also demonstrated

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* *Trans. Faraday Soc.*, 1939, 35, 163.

that perfectly pure BN is only very faintly flame-luminescent but addition of trace of carbon (1 in 500 to 1 in 10,000) makes it strongly luminescent. It is suggested that C being close in periodic table to B and to N is a suitable atom to form active centres in the lattice of the crystal (*cf.* Cu in ZnS).[43] Zinc sulphide and silicate (Willemite) are strongly luminescent.[41]

**Variation of Luminescence with Temperature** (p. 166).—Paneth and Winternitz [42] suggest that flame performs two functions—to heat and to activate. If specimen has been activated by flame, electrical heating immediately afterwards will produce luminescence. Boron nitride is luminescent up to a bright red heat ; when placed in a carbon boat heated electrically to redness, a flame caused it to luminesce blue with much greater intensity. There is, however, no reference to luminescence at higher temperatures than this.

**Quality of Light Emitted** (p. 167).—Tiede and Tomaschek [39] claim to have established the identity of the luminescent radiation emitted by BN under stimulus of flame and of cathode rays. The similarity of the spectral distribution of the light emitted under these stimuli from

$$CaO + \text{trace Bi, or } CaO + \text{trace Mn,}$$

has also been demonstrated.[41] Tiede and Tomaschek in a later paper [43] showed that the effect of varying the proportion of activating C in boron nitride was to alter the intensity of the spectral bands but not their position. Careful comparison is made between these results obtained by excitation with ultra-violet light, cathode rays (in air) and hydrogen flame. In the latter case bands are less well defined and appear to be displaced 5-10 $m\mu$ towards the long-wave end.[43]

**Possible Mechanisms** (p. 167).—Donau suspected an oxidation-reduction process was responsible for the luminescence, but admitted that a specimen of CaO showed no loss in weight on a micro-balance after exposure to flame. The three subsequent papers, however, all reject this explanation, and Paneth suggests bombardment of free ions, or perhaps electrons, from the flame may well be responsible. Tiede and Buscher claimed that ZnS and Willemite would luminesce even when a thin wall of fused silica was interposed between the specimen and the flame. This suggests ultra-violet radiation as the exciting agent, but no definite conclusions are arrived at.

Several workers have also observed [45] that a momentary luminescence is caused by the impingement of a jet of active nitrogen on some substances, and Tiede and Schleede pointed out [46] that the phenomenon resembled flame-excited luminescence. With both forms of excitation some well-known luminescent substances, e.g., Sidot Blende, fail to respond, and in general the effect is most noticeable with compounds of elements of low atomic weight, e.g. LiF, $BeCO_3$, BN, $Ca(N_3)_2$. From this analogy it would appear that a further possible explanation of the phenomenon is to be found in the specification of the substances in de-activating the active gas molecules in the flame.

In the light of these papers, it is no longer possible to doubt the reality of this phenomenon, at least as far as the transitory phenomenon at low temperatures is concerned.

Really satisfactory evidence for the existence of a permanent luminescence at temperatures above red heat is still, however, lacking.

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[39] Tiede and H. Tomaschek, *Z. Elektrochem.*, 1923, **29**, 303.

[40] Donau, *Monatsheft Chem.*, 1913, **34**, 949 ; *Wien: Sit.*, 1913, **122**, 335.

[41] Tiede and Buscher, *Ber.*, 1920, **53**, (2), 2206.

[42] Paneth and Winternitz, *Ber.*, 1918, **51**, (2), 1728.

[43] Tiede and H. Tomaschek, *Z. anorg. Chem.*, 1925, **147**, 111.

[44] Balmain, *Phil. Mag.*, 1842, **21**, 270 and subsequent papers up to *l.c.* 1846, **25**, 87.

[45] Lewis, *Nature*, 1923, **111**, 529. Jevons, *ibid.*, p. 705.

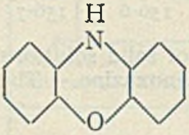
[46] Tiede and Schleede, *Naturwiss*, 1923, **11**, 765.

# ISOMORPHOUS RELATIONSHIPS OF SOME ORGANIC COMPOUNDS OF ANALOGOUS CONSTITUTION.

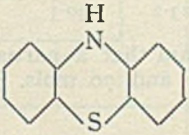
By N. M. Cullinane and W. T. Rees.

*Received 4th December*, 1939.

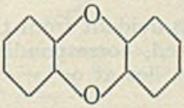
In a previous paper[1] the isomorphous relationships of a number of heterocyclic compounds of similar constitution were investigated, the ability of binary mixtures of these substances to yield solid solutions being chosen as the criterion of isomorphism. The work has now been extended, the compounds examined including phenoxazine (I), phenthiazine (thiodiphenylamine) (II), diphenylene dioxide (III), phenoxthionine (IV), and thianthren (V). The results indicate that analogously constituted derivatives of elements of similar type form solid solutions, provided that their spatial structures are also alike.



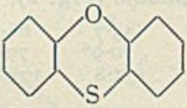
(I)



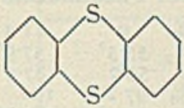
(II)



(III)



(IV)



(V)

Simultaneously with this work an X-ray, crystallographic, and optical investigation of these substances is being carried out by Mr. R. G. Wood and his collaborators of the Physics Department of this College, and their results will shortly be published elsewhere.

## Experimental.

### Preparation and Purification of Materials.

**Phenoxazine** was prepared by condensing catechol and *o*-aminophenol in the presence of a little of the aminophenol hydrochloride.[2] Recrystallisation from hot dilute alcohol, followed by sublimation, yielded colourless leaflets, m.p. 156·7°.

The commercial sample of **phenthiazine** was very impure, but when it was boiled for 3 hours with 30 % aqueous sodium hydroxide, washed with water, then sublimed and recrystallised from alcohol, a pure product was obtained, consisting of pale yellow leaflets, m.p. 184·4°. Previous investigators[3] give the m.p. as 180°.

The purification of **diphenylene dioxide** (m.p. 119·9°), **thianthren** (m.p. 156·7°), and **diphenylene oxide** (m.p. 82·4°) have been already described.[1]

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[1] Cullinane and Plummer, *J. Chem. Soc.*, 1938, 63.

[2] Kehrmann and Neil, *Ber.*, 1914, **47**, 3107.

[3] Holzmann, *Ber.*, 1888, **21**, 2065; Knoevenagel, *J. prakt. Chem.*, 1914, [ii], **89**, 12.

**Phenoxthionine**, prepared by the action of sulphur on diphenyl ether in the presence of anhydrous aluminium chloride,[4] was extracted thoroughly with 30 % aqueous sodium hydroxide solution, washed with water, recrystallised from alcohol, sublimed, and again recrystallised from the same solvent, giving white needles, m.p. 55·7°.

The commercial specimen of **carbazole** was recrystallised from boiling acetone, sublimed, and again recrystallised. Colourless leaflets, m.p. 245·8°, were obtained.

## Results.

Thaw points ($T_1$) and melting temperatures ($T_2$) were determined by the method described in a previous memoir.[1] For the purified compounds $T_1$ and $T_2$ did not differ by more than 1°.

A selection of the results is shown graphically in Figs. 1-5, and the complete data are tabulated below.

**System Phenoxazine-Diphenylene Dioxide (Fig. 1).**

| | | | | | | |
|---|---|---|---|---|---|---|
| Phenoxazine, mols. % | 0 | 9·7 | 16·5 | 22·6 | 29·7 | 35·2 |
| $T_1$ . . . | 119·4° | 105·2° | 100·4° | 96·0° | 90·1° | 90·3° |
| $T_2$ . . . | 119·9 | 117·2 | 114·3 | 111·8 | 107·9 | 93·9 |
| Phenoxazine, mols. % | 39·2 | 51·4 | 70·9 | 79·2 | 87·9 | 100 |
| $T_1$ . . . | 90·2° | 89·8° | 91·5° | 98·2° | 114·1° | 156·0° |
| $T_2$ . . . | 101·2 | 123·2 | 140·1 | 145·3 | 150·6 | 156·7 |

It is evident from the diagram that a partial series of solid solutions is formed, corresponding to 30 and 70 mols. % of phenoxazine. The eutectic lies at 90°.

**System Phenthiazine-Phenoxthionine (Fig. 2).**

| | | | | | | |
|---|---|---|---|---|---|---|
| Phenthiazine, mols % | 0 | 11·3 | 29·2 | 53·7 | 66·1 | 83·2 |
| $T_1$ . . . | 55·3° | 57·6° | 62·3° | 70·9° | 79·4° | 100·3° |
| $T_2$ . . . | 55·7 | 87·3 | 123·6 | 151·8 | 163·8 | 175·9 |
| Phenthiazine, mols. % | 97·2 | 100 | | | | |
| $T_1$ . . . | 140·2° | 183·6° | | | | |
| $T_2$ . . . | 183·3 | 184·4 | | | | |

The curve reveals a complete series of solid solutions, the melting-points of all mixtures lying between those of the pure components.

**System Phenoxazine-Phenthiazine (Fig. 3).**

| | | | | | | |
|---|---|---|---|---|---|---|
| Phenoxazine, mols. % | 0 | 11·8 | 17·6 | 36·0 | 48·3 | 68·9 |
| $T_1$ . . . | 183·6° | 148·3° | 143·7° | 139·8° | 140·4° | 139·9° |
| $T_2$ . . . | 184·4 | 178·8 | 176·3 | 164·9 | 156·9 | 142·6 |
| Phenoxazine, mols. % | 73·5 | 74·4 | 87·1 | 94·1 | 100 | |
| $T_1$ . . . | 139·7° | 140·0° | 139·8° | 142·1° | 156·0° | |
| $T_2$ . . . | 142·0 | 143·5 | 151·1 | 154·1 | 156·7 | |

The system exhibits a eutectic at 140°, with a partial series of solid solutions, of compositions 22 and 93 mols. % of phenoxazine.

**System Diphenylene Dioxide-Phenoxthionine (Fig. 4).**

| | | | | | | |
|---|---|---|---|---|---|---|
| Phenoxthionine, mols. % | 0 | 5·7 | 26·1 | 43·9 | 66·3 | 73·0 |
| $T_1$ . . . | 119·4° | 46·7° | 46·8° | 46·7° | 46·5° | 46·5° |
| $T_2$ . . . | 119·9 | 117·7 | 106·9 | 94·4 | 75·0 | 62·6 |
| Phenoxthionine, mols. % | 78·2 | 90·4 | 94·8 | 100 | | |
| $T_1$ . . . | 46·4° | 46·6° | 46·7° | 55·3° | | |
| $T_2$ . . . | 47·2 | 52·3 | 53·9 | 55·7 | | |

A simple eutectic is shown here, with negligible solid solution formation. The eutectic point is 46·5°, corresponding to 78 mols. % of phenoxthionine.

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[4] Suter, McKenzie and Maxwell, *J. Amer. Chem. Soc.*, 1936, **58**, 718.

**System Phenoxthionine-Thianthren.**

| | | | | | | |
|---|---|---|---|---|---|---|
| Phenoxthionine, mols. % | 0 | 10·0 | 30·1 | 48·7 | 69·2 | 81·1 |
| $T_1$ . . . | 155·9° | 52·0° | 51·9° | 51·7° | 51·2° | 51·6° |
| $T_2$ . . . | 156·7 | 153·6 | 142·1 | 126·3 | 105·5 | 84·2 |
| Phenoxthionine, mols. % | 90·0 | 93·0 | 95·4 | 100 | | |
| $T_1$ . . . | 51·4° | 51·9° | 51·8° | 55·3° | | |
| $T_2$ . . . | 64·0 | 52·9 | 55·1 | 55·7 | | |

This curve also shows a simple eutectic, at 52°, corresponding to 93 mols. % of phenoxthionine, without any formation of solid solution.

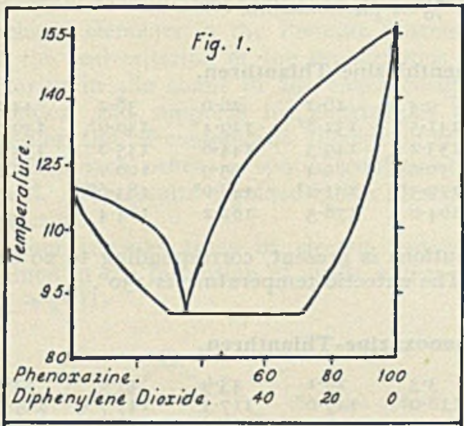


Fig. 1.

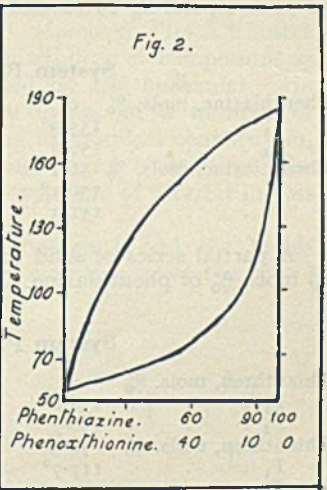


Fig. 2.

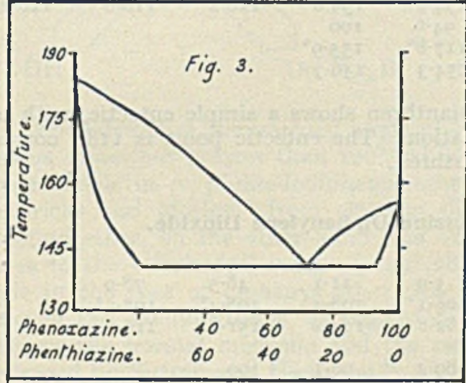


Fig. 3.

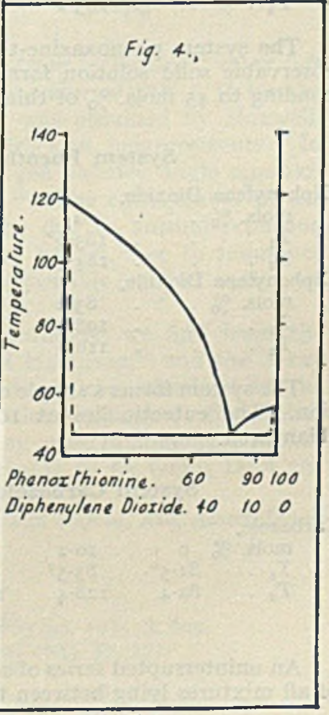


Fig. 4.

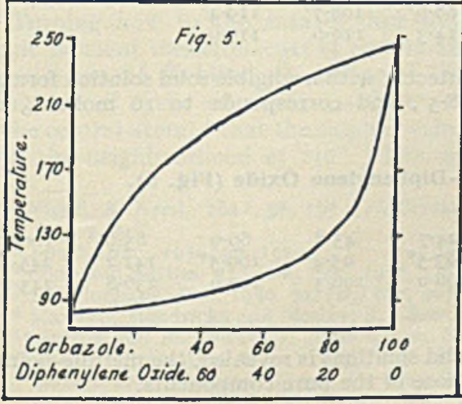


Fig. 5.

*Legends to abscissae give mols. %.*

### System Phenoxazine-Phenoxthionine.

| Phenoxazine, mols. % | 0 | 2·6 | 6·7 | 10·2 | 16·6 |
|---|---|---|---|---|---|
| $T_1$ | 55·3° | 50·3° | 50·5° | 50·1° | 50·1° |
| $T_2$ | 55·7 | 55·3 | 54·0 | 51·2 | 65·1 |
| Phenoxazine, mols. % | 22·9 | 49·2 | 78·9 | 94·3 | 100 |
| $T_1$ | 50·2° | 49·9° | 50·6° | 50·4° | 156·0° |
| $T_2$ | 76·6 | 115·2 | 142·7 | 153·8 | 156·7 |

The system reveals a simple eutectic, the eutectic temperature being 50°, corresponding to 10 mols. % of phenoxazine.

### System Phenthiazine-Thianthren.

| Phenthiazine, mols. % | 0 | 9·4 | 16·2 | 26·0 | 38·2 | 44·1 |
|---|---|---|---|---|---|---|
| $T_1$ | 155·9° | 141·5° | 132·8° | 129·4° | 130·0° | 130·0° |
| $T_2$ | 156·7 | 153·2 | 149·5 | 144·8 | 135·8 | 134·4 |
| Phenthiazine, mols. % | 56·1 | 70·9 | 89·4 | 95·9 | 100 | |
| $T_1$ | 130·1° | 129·5° | 131·2° | 148·0° | 183·6° | |
| $T_2$ | 151·3 | 164·6 | 178·5 | 182·2 | 184·4 | |

A partial series of solid solutions is present, corresponding to 20 and 89 mols. % of phenthiazine. The eutectic temperature is 130°.

### System Phenoxazine-Thianthren.

| Thianthren, mols. % | 0 | 3·3 | 24·1 | 43·9 | 45·8 | 53·1 |
|---|---|---|---|---|---|---|
| $T_1$ | 156·0° | 118·0° | 117·6° | 117·5° | 117·7° | 117·5° |
| $T_2$ | 156·7 | 154·9 | 139·0 | 120·2 | 118·8 | 126·2 |
| Thianthren, mols. % | 74·9 | 94·6 | 100 | | | |
| $T_1$ | 117·7° | 117·8° | 155·9° | | | |
| $T_2$ | 143·2 | 154·3 | 156·7 | | | |

The system phenoxazine-thianthren shows a simple eutectic, with no observable solid solution formation. The eutectic point is 118°, corresponding to 45 mols. % of thianthren.

### System Phenthiazine-Diphenylene Dioxide.

| Diphenylene Dioxide, mols. % | 0 | 5·0 | 21·1 | 48·5 | 78·0 |
|---|---|---|---|---|---|
| $T_1$ | 183·6° | 108·1° | 108·3° | 108·4° | 108·3° |
| $T_2$ | 184·4 | 182·8 | 174·2 | 151·8 | 116·6 |
| Diphenylene Dioxide, mols. % | 83·2 | 89·2 | 98·1 | 100 | |
| $T_1$ | 108·5° | 108·6° | 108·7° | 119·4° | |
| $T_2$ | 110·0 | 114·3 | 119·6 | 119·9 | |

The system forms a simple eutectic, with negligible solid solution formation. The eutectic lies at 108·5°, and corresponds to 16 mols. % of thianthren.

### System Carbazole-Diphenylene Oxide (Fig. 5).

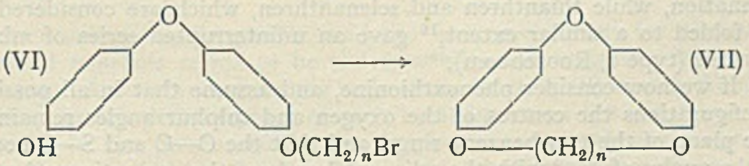
| Carbazole, mols. % | 0 | 10·2 | 24·7 | 43·8 | 66·9 | 85·9 | 100 |
|---|---|---|---|---|---|---|---|
| $T_1$ | 81·5° | 83·5° | 87·5° | 95·4° | 109·5° | 141·2° | 245·1° |
| $T_2$ | 82·4 | 128·4 | 166·0 | 196·3 | 219·6 | 236·8 | 245·8 |

An uninterrupted series of solid solutions is revealed, the melting-points of all mixtures lying between those of the pure components.

## Discussion of Results.

Recent investigations suggest that the phenomenon of isomorphism is connected with similarity in molecular configuration rather than chemical constitution. Thus in the view of Niggli [5] the ability to form solid solutions is due to similarity rather of geometrical form than of chemical behaviour. He points out that only in so far as atoms are sufficiently closely related chemically to yield geometrically similar types of compounds will isomorphism be predominantly connected with groups of related elements in the Periodic System. Moreover Pirsch [6] states that the real criterion of the isomorphous miscibility of compounds is similarity in the shape of the space occupied by the molecules. He concludes, and supports his conclusions by means of a number of examples, that if compounds, though differing in chemical constitution, approach each other in spatial configuration, mixed crystals will be formed. The results obtained in the present work are of interest in this connection.

From considerations of electric dipole moment,[7] and the yields obtained in the formation of cyclic ethers by ring closure of the type [8] (VI) → (VII)



it is concluded that the valency angle of oxygen in diphenyl ether has a value somewhat greater than 120°, while a value of 118 ± 3° for the oxygen angle in *p* : *p'*-diiododiphenyl ether was obtained by Maxwell, Hendricks and Mosley [9] from electron diffraction measurements. In dimethyl ether, on the other hand, the oxygen valency angle approximates to the tetrahedral value of 109° 28'.[10] The enlargement of the angle in the case of diphenyl ether may be due to mutual repulsion between the phenyl groups, as suggested by Stuart,[11] or to resonance between the normal molecule and the two possible excited states, as envisaged by Sutton and Hampson.[12]

Turning now to the case of diphenyl sulphide, we find from the dipole moment measurements of Sutton and Hampson,[12] and the X-ray experiments of Kohlhaas,[13] confirmed by the yields obtained in the formation of cyclic ethers of the type mentioned above (with sulphur as the central atom),[8] that the sulphur valency angle in diphenyl sulphide is in the neighbourhood of 112°. This appears to be larger than the

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[5] Niggli, *Z. Krist.*, 1921, **56**, 167 ; *cf.* Ferrari and Baroni, *Atti. Accad. Lincei* 1928, [vi], **7**, 848.

[6] Pirsch, *Ber.*, 1936, **69**, 1323.

[7] Coop and Sutton, *J. Chem. Soc.*, 1938, 1869.

[8] Lüttringhaus, *Ber.*, 1939, **72**, [*B*], 887, 907.

[9] Maxwell, Hendricks and Mosley, *J. Chem. Physics*, 1935, **3**, 699.

[10] Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 477.

[11] Stuart, *Z. physikal Chem.*, 1937, *B*, **36**, 155.

[12] Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 953.

[13] Kohlhaas and Lüttringhaus, *Ber.*, 1939, **72**, [*B*], 897.

corresponding angle in hydrogen sulphide[14] or dimethyl sulphide,[15] and can be accounted for in the same way as in the case of diphenyl ether.

Apropos of this stereo-chemical dissimilarity between diphenyl ether and sulphide, the fact that these substances form only a limited series of solid solutions may be noted. Furthermore, according to Thompson and Turner,[16] the preferred valency angle of selenium is very close to that of sulphur, and Pascal[17] has shown that diphenyl sulphide and selenide give a continuous series of solid solutions (type III, Roozeboom).[18]

In diphenylene oxide and sulphide the heterocyclic atoms form part of a rigid system, and a closer similarity in the valency angles than in the corresponding diphenyl derivatives is probably enforced. The system diphenylene oxide-sulphide thus exhibits a complete series of mixed crystals[1] (type III, Roozeboom).[18]

Diphenylene dioxide possesses a planar molecule, as evidenced by the fact that it has zero dipole moment.[19] This is confirmed by the experiments of Wood, which show that the molecule probably has a centre of symmetry, which would be impossible if it were folded. The corresponding sulphur compound thianthren, on the other hand, with a large moment, is folded along the S—S axis.[20] In this connection it may be noted that Cullinane and Plummer[1] found that the system diphenylene dioxide-disulphide formed a eutectic with negligible solid-solution formation, while thianthren and selenanthren, which are considered to be folded to a similar extent,[16] gave an uninterrupted series of mixed crystals (type I, Roozeboom).[18]

If we now consider phenoxthionine, and assume that in all possible configurations the centres of the oxygen and sulphur angles remain in the plane of the two benzene rings, and that the O—C and S—C bonds make angles of 120° with the adjacent bonds of the aromatic nucleus,[16] taking the radii of aromatic carbon, oxygen, and sulphur to be 0·7, 0·66, and 1·05 A. respectively, we obtain the following relationships between the oxygen angle, the sulphur angle, and the angle of fold about the O—S axis :

| | | | | | |
|---|---|---|---|---|---|
| O angle . . . . | 100° | 110° | 120° | 130° | 133° |
| S angle . . . . | 84° | 92° | 99° | 105° | 107° |
| Angle of fold . . . . | 113° | 127° | 142° | 162° | 180° |

As it is unlikely that oxygen would tolerate a greater angle than 130°, we conclude that the molecule is folded.

The results obtained in the present work show that the planar diphenylene dioxide forms a eutectic with phenoxthionine (Fig. 4) without any appearance of mixed crystal formation. Moreover, Wood's experiments show that there is a pronounced dissimilarity in the structures of the two substances.

Not much is known concerning the preferred valency angle of

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[14] Cross, *Physical Rev.*, 1935, **47**, 7 ; Dadieu and Kohlrausch, *Physikal. Z.*, 1932, **33**, 165.

[15] Pai, *Ind. J. Physics*, 1934, **9**, 121 ; Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2040.

[16] Thompson and Turner, *J. Chem. Soc.*, 1938, 30.

[17] Pascal, *Bull. Soc. chim.*, 1912, **11**, 30.

[18] Roozeboom, *Z. physikal. Chem.*, 1899, **30**, 385.

[19] Bennett, Earp and Glasstone, *J. Chem. Soc.*, 1934, 1180.

[20] Bennett and Glasstone, *J. Chem. Soc.*, 1934, 128 ; *cf.* Bergmann, *Ber.*, 1932, **65**, 457.

nitrogen, although in ammonia[21] and trimethylamine[22] it appears to approximate to the tetrahedral value. In diphenylamine the same type of resonance can occur as in diphenyl ether, and this would cause an enlargement of the nitrogen angle, though to what extent is not known. In 9 : 10-dihydrophenazine and its derivatives, where resonance can also occur, Sutton and Hampson[12] suggest that the molecule is planar as in diphenylene dioxide. On the other hand Campbell, Le Fèvre, Le Fèvre and Turner[23] are of opinion that 9 : 10-dihydro- and 9 : 10-dimethyl dihydro-phenazine, which appear to have definite though small dipole moments, are folded.

Phenazine itself, however, which possesses zero dipole moment, is undoubtedly flat,[23] as would be expected from the widening of the nitrogen angle due to the presence of the double bond, a conclusion confirmed by Wood.

Making the same assumptions in the case of phenthiazine as for phenoxthionine, and taking the radius of the nitrogen atom as 0·7 A., we obtain the following relationships between the nitrogen angle, the sulphur angle, and the angle of fold about the N—S axis :

| | | | | | |
|---|---|---|---|---|---|
| N angle . . . | 100° | 110° | 120° | 130° | 132° |
| S angle . . . . | 85° | 93° | 100° | 107° | 108° |
| Angle of fold . . . | 114° | 128° | 143° | 166° | 180° |

As a valency angle greater than 130° is scarcely likely for nitrogen, a folded molecule seems to be the most plausible structure for phenthiazine. A nonplanar molecule is shown to be compatible with Wood's results, though definite proof of such a configuration has not been obtained. In the present work, the temperature-concentration diagram (Fig. 2) shows that the system phenthiazine-phenoxthionine exhibits an unbroken series of mixed crystals (type I, Roozeboom).[18] Moreover, the system diphenylene dioxide-phenthiazine forms a eutectic, no solid solution being present.

In the case of phenoxazine, we obtain the following relationships between the nitrogen angle, the oxygen angle, and the angle of fold about the N—O axis :

| | | | |
|---|---|---|---|
| N angle . . . . . . . . | 100° | 110° | 119° |
| O angle . . . . . . . . | 102° | 112° | 121° |
| Angle of fold . . . . . . . | 126° | 145° | 180° |

The above results suggests that there is only slight, if any, folding of the molecule. The systems diphenylene dioxide-phenoxazine (Fig. 1) and phenthiazine-phenoxazine (Fig. 3) both reveal a limited series of solid solutions (type V, Roozeboom).[18]

Referring now to the corresponding carbon compounds, in methane the carbon valency angle has the tetrahedral value of 109° 28′. Furthermore Lüttringhaus[8] concludes from his ring closure experiments that the central carbon angle in diphenyl methane is 110 ± 3°, so that there is no appreciable enlargement. The fact that no resonance effect is possible in this compound, such as that proposed, for example, in the case of diphenyl ether, would account for the absence of any pronounced

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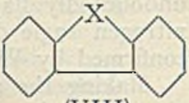
[21] Dennison and Uhlenbeck, *Physical Rev.*, 1932, 41, 313 ; Lueg and Hedfeld, *Z. Physik*, 1932, 75, 599.

[22] Brockway and Jenkins, *loc. cit.*[15]

[23] Campbell, Le Fèvre, Le Fèvre and Turner, *J. Chem. Soc.*, 1938, 407 ; *cf.* Bergmann, Engel and Meyer, *Ber.*, 1932, 65, 446.

alteration in the angle. In this connection the fact that diphenyl methane and diphenyl ether form a eutectic, without any mixed crystals being formed, is noteworthy.[24]

Now 9 : 10-dihydroanthracene appears to have a measureable dipole moment,[23] indicating that its molecule is folded about the $CH_2$—$CH_2$ axis, as is to be expected if the carbon valency angles are less than 120°. On the other hand, anthracene possess a planar structure,[25] and this can be explained by the carbon angles of the centre ring being increased owing to the double bonds attached to them. Moreover, anthracene and its dihydro-derivative give a eutectic, no solid solution being observed.[26]



(VIII)

As already mentioned, compounds of the type (VIII) possess a fairly rigid structure, and though X may vary, a similar valency angle is probably enforced. Thus the systems fluorene-diphenylene oxide,[24] carbazole-diphenylene oxide, diphenylene oxide-diphenylene sulphide,[1] and diphenylene sulphide-diphenylene selenide [1] all yield continuous series of solid solutions.

The authors acknowledge their indebtedness to the Committee of the van't Hoff Fund and to the Chemical Society for grants.

*Tatem Laboratories, University College,*
*Cardiff.*

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[24] Lüttringhaus, *Annalen*, 1937, 528, 229.
[25] Robertson, *Proc. Roy. Soc.*, 1933, 140, 79.
[26] Grimm, Günther and Tittus, *Z. physikal. Chem.*, 1931, *B*, 14, 210.

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## REVIEWS OF BOOKS.

**Der Disperse Bau der Festen Systeme.** By DR. D. BALAREW. (Dresden and Leipzig : Theodor Steinkopf. Pp. vi + 240, with 45 illustrations. Price, R.M. 7.50 : bound, R.M. 8.62.)

This book sets out to discuss the nature of "impurity" in the solid state, and therefore deals in considerable detail with the properties of the "real" and the "ideal" crystal. Borderland phrases like amorphous bodies and super-cooled liquids receive attention in much the same way. There is also an interesting section upon velocity of crystallisation, both spontaneous and linear. The former is of dimensions Number of grains/Time, whereas the latter is Length/Time, and thus more truly a velocity in the normal sense.

A good feature is the resumé at the end of each chapter, which helps to balance to some extent the tendency to "write round the references." But the specialist will welcome Professor Balarew's work for reference purposes, and for its thoroughness.

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