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## THE DUHEM-MARGULES EQUATION AND RAOULT'S LAW.

By C. R. Bury.<br>Received 20th March, 1940.

The thermodynamical treatment of the Duhem-Margules equation, and of Raoult's law of partial vapour pressures, given in most textbooks on the subject is misleading or inaccurate. The basis of the discussion is the Gibbs-Duhem equation

$$
-S \mathrm{~d} T+V \mathrm{~d} P-\sum_{i} n_{i} \mathrm{~d} \mu_{i}=0
$$

recommended symbols being used. A system of any number of components and two phases in equilibrium with each other, a liquid and a gas phase, is considered. If the perfect gas laws be assumed valid, the chemical potential ( $\mu_{i}$ ) of cach component in the gas phase is related to its partial pressure ( $P_{i}$ ) by the equation

$$
\left(\frac{\partial \mu_{i}}{\partial \log P_{i}}\right)_{T}=R T
$$

Since the potentials of a component must be the same in the two phases if the system is in equilibrium, one can write for the liquid phase

$$
\begin{equation*}
\mathrm{d} T=0, \mathrm{~d} P=0, R T \sum_{i} n_{i} \mathrm{~d} \log P_{i}=0 \tag{I}
\end{equation*}
$$

On dividing by $R T \sum_{i} n_{i}$,

$$
\sum_{i} N_{i} \mathrm{~d} \log P_{i}=0
$$

which is the Duhem-Margules equation. The simplest integral solution of this is a set of equations, one for each component, of the type

$$
P_{i}=N_{i} P_{i}{ }^{0}
$$

where $P_{i}{ }^{0}$ is the vapour pressure of the pure liquid component $i$. This is Raoult's law of partial vapour pressures.

Now for a system of $x$ components, the Duhem-Margules equation appears, and is usually taken to be, a relation between the $x$ quantities $\mathrm{d} \log P_{i}$, such that any $x-\mathrm{I}$ of these may be assigned arbitrary values when the remaining quantity becomes fixed. There is, however, a further restriction, which is generally neglected, comprised in the equation $\mathrm{d} P=0$, which has been assumed in deducing equation ( I ). From another point of view, the point of view of the phase rule, for a system of $x$ components and 2 phases, $T$ and $P$ being fixed, there are only $x-2$ further degrees of freedom. For a two-component system, to which the Duhem-Margules equation is most commonly applied, there are no further degrees of freedom, and the equation is meaningless, except in special cases (maxima and minima in vapour pressure curves).

To derive an equation of more general validity, it is necessary to give up the restriction $\mathrm{d} P=0$, and, instead of equation (I), to write

$$
\mathrm{d} T=0, V \mathrm{~d} P-R T \sum n_{i} \mathrm{~d} \log P_{i}=0 .
$$

On dividing by $R T \sum_{i}$, since $V=\sum_{i} n_{i} V_{i}$ (where $V_{i}$ is the partial molar volume of the component $i$ ) and since $\mathrm{d} P=\sum_{i} \mathrm{~d} P_{i}$,

$$
\begin{equation*}
\frac{\sum N_{i} V_{i}}{R T_{i}} \sum_{i} P_{i}-\sum_{i} N_{i} \mathrm{~d} \log P_{i}=0 \tag{2}
\end{equation*}
$$

This more general equation replaces the Duhem-Margules equation, which it includes as a special case.

The set of equations which comprise Raoult's law do not satisfy this equation, except in the special case $P_{a}{ }^{0}=P_{b}{ }^{0}=\ldots=P_{x}{ }^{0}$. Ideal solutions have been defined as solutions that obey Raoult's law at all temperatures and pressures. In that case, only liquids that have the same vapour pressures at all temperatures can form ideal solutions when they are mixed.

In determining partial vapour pressures of the $x$ components of a solution by the dynamic method, an additional component-an inert gas $y$-is admitted to the system. No control is exercised over the pressure of $y$, but the experimental conditions ensure that the total pressure remains constant at some standard value, usually atmospheric pressure. The system is now an $(x+1)$-component system; the restriction of the variation of pressures of the first $x$ components imposed by the condition $\mathrm{d} P=0$ no longer operates. In general, the addition of an extra component will make the mathematical treatment more complex, but if the gas $y$ is insoluble in the liquid, the Duhem-Margules equation will hold rigidly for the original $x$ components of the solution, while the additional component-present in the gas phase only-enables the pressure to be maintained constant without the corresponding restrictions on the variation of pressures that characterised the original $x$-component system. Under these conditions, Raoult's law becomes possible in the general case $P_{a}{ }^{0} \neq P_{b}{ }^{0} \neq \ldots \neq P_{x}{ }^{0}$.

It is, however, necessary to distinguish between $P_{i}$, the partial pressure of the component $i$ in the vapour phase of the $x$-component system where the total pressure $P=\sum_{i} P_{i}$, and $P_{i}^{\prime}$, the pressure of the same component in the ( $x+\mathrm{I}$ )-component system when the admission of $y$ has raised the pressure to the standard pressure $P^{\prime}=\sum_{i} P_{i}{ }^{\prime}+P_{\nu}{ }^{\prime}$. Similarly, $P_{i}{ }^{0}$ must be distinguished from $P_{i}{ }^{0}$. Raoult's law for the $x$ condensable components of the ( $x+1$ )-component system must be expressed by the set of equations

$$
\begin{equation*}
P_{i}^{\prime}=N_{i} P_{i}{ }^{0} \tag{3}
\end{equation*}
$$

The dependence of $P_{i}^{\prime}$ on $P^{\prime}$ is given by the equation ${ }^{1}$

$$
\left(\frac{\partial \log P_{i}^{\prime}}{\partial P^{\prime}}\right)_{T n_{a} \ldots n_{x}}=\frac{V_{i}}{R T}
$$

Assuming $V_{i}$ to be independent of pressure, which is justifiable for the small changes of pressure usually involved, integration gives

$$
\log P_{i}=\log P_{i}^{\prime}+\frac{V_{i}\left(P_{i}-P^{\prime}\right)}{R T} ;
$$

${ }^{1}$ See, for example, Guggenheim, Modern Thermodynamics, 1933, p. So.
similarly,

$$
\log P_{i}{ }^{0}=\log P_{i}{ }^{{ }^{\prime}}+\frac{V_{i}\left(P_{i}{ }^{0}-P^{\prime}\right)}{R T}
$$

Using these two equations to eliminate $P_{i}^{\prime}$ and $P_{i}{ }^{0}$ from equation (3), assuming $V_{i}$ to be independent of concentration, gives
or

$$
\left.\begin{array}{c}
\log P_{i}=\log N_{i}+\log P_{i}{ }^{0}+\frac{V_{i}\left(\sum_{i} P_{i}-P_{i}{ }^{0}\right)}{R T}  \tag{4}\\
P_{i}=N_{i} P_{i} \mathrm{e}^{{ }^{0}\left(\frac{V_{i}}{i\left(P_{i}-P_{i}\right)}\right.} \boldsymbol{R T}
\end{array}\right\}
$$

The addition of an inert gas to the system is a subject of interest in itself, but has here only been used to derive a relation between partial pressures and mol fractions in the $x$-component system; a relation which is independent of the existence in practice of an inert gas absolutely insoluble in the liquid. This equation is essentially the same as the equation

$$
P_{i}=N_{i} P_{i}{ }^{0} \mathrm{e}^{-\frac{1}{\mathrm{~B}}\left(v_{i}-\varphi_{i}\right)},
$$

where $\psi$ is equivalent to $\mu / T$, deduced by van Laar, ${ }^{2}$ but in this form the relation between this equation and equation (2) is not obvious. A set of equations (4) satisfies equation (2), and is the simplest integral solution of (2) ; i.e., a set of equations (4) is the simplest law for the dependence of partial vapour pressures on concentration in a mixture of liquids, the vapour pressures of which are not all equal.

The term $V_{i}\left(\Sigma P_{i}-P_{i}{ }^{0}\right) / R T$ will usually be very small, and partial vapour pressures calculated from equation (4) will generally be indistinguishable from those calculated from Raoult's law.

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${ }^{2}$ Z. physik. Chem., 1895, 18, 258; see also Schottky, Thermodynamik, 1929, 384.

## THE INFRA-RED SPECTRUM OF DIMETHYL ZINC.

By H. W. Thompson, J. W. Linnett and F. J. Wagstaffe.
Received I4th May, 1940.
Although several measurements of the Raman spectra of metal alkyls have been described, the infra-red spectra of these interesting compounds do not appear to have received corresponding attention. The only infra-red data reported are those of Kettering and Sleator ${ }^{1}$ on some tetra-alkyls of tin, lead and germannium. The present paper summarises measurements on dimethyl zinc, using low dispersion. The most important information sought in the work was a knowledge of the vibration frequencies and their correlation with the various normal modes. These data have interesting applications; definite assignment

[^0]of all the vibration frequencies may lead to important inferences about the bond force constants and molecular structure, and may make a calculation of the thermodynamic functions possible. Again, much interest has recently been shown in the phenomenon of internal rotation in molecules, especially about the carbon-carbon bond. A correlation of specific heat data with the measured vibration frequencies suggests that whereas in ethane ${ }^{2}$ the internal rotation may be considerably restricted, in dimethyl acetylene it may be entirely frec. ${ }^{3}$ It would be interesting to discover whether the two methyl groups in dimethyl zinc can rotate internally with respect to each other; if this is not so, the spectroscopic data may give us some indication of the value of the restricting potential.

The Raman spectrum of dimethyl zinc has been studied by Venkateswaran ${ }^{4}$ and by Pai. ${ }^{5}$ The ultra-violet spectrum was previously measured by Thompson and Linnett. ${ }^{6}$

## Experimental.

The spectrometer was the large aperture Hilger instrument D 88 with $f 4.5$, having interchangcable prisms of quartz, fluorite, rock salt and sylvine, and Wadsworth mounting. For comparable slit widths the resolving power of this instrument compared with most other prism spectrometers is high. The two concave mirrors are each 23 cm . focal length and 5 cm . in diameter, and the prisms are each about 45 mm . in height and 74 mm . length of refracting face. The instrument was modified so that the thermocouple (linear junction ro $\mathrm{mm} . \times 0.5 \mathrm{~mm}$.) could be used in vacuo. For this purpose the radiation emerged from the second slit onto a concave gold-surfaced mirror of approximately to cm . radius of curvature, rotated slightly about a vertical axis so that the reflected beam fell upon a plane aluminised mirror and thence was focussed on the junctions of the thermocouple. The latter was enclosed in an evacuated metal box with rock salt window. By setting the mirrors so that the beam was reflected only slightly off-axis of the concave mirror, little distortion of the image emerging from the second slit was produced, and the thermocouple box could be set so that the linear image fell along the line of the thermocouple junctions. The instrument was first set up visually with sodium D light, and the readings on the wave-length drum were then checked, using the thermocouple and galvanometer against ammonia absorption bands at $1.967 \mu$ and $2.26 \mu$. The Wadsworth mirror was then slightly rotated as required by means of an adjusting screw so that the drum read accurately. The settings were then checked at various points over the spectrum against known bands of water, carbon dioxide, carbon disulphide and ethylene. The entire instrument was enclosed in a blackened wooden box. The drum could be rotated from outside the box by means of a long arm, and read through a glass window.

The source of radiation was a 4 cm . length of Globar rod fitting at each end into iron sockets, held vertically between spring clips. The latter were fixed to large copper blocks. The Globar was heated electrically from the mains and when burning at its maximum consumed about 6 amp . No precautions were taken to ensure a constant voltage supply, but it is certain that no errors were introduced in this way, since all bands were checked several, and in special cases, many times. The radiation was

[^1]reflected on to the entrance slit by a concave aluminised mirror of long focal length placed near the Globar. Two absorption cells were used, one evacuated as a blank, and readings were taken alternately through each cell at each wave-length. The two cells were also checked against each other when evacuated. The cells were glass tubes 21 cm . in length and 3 cm . in diameter; at their ends were thin metal plates, fixed with wax, and having circular apertures. The rock salt ends were pressed on to these metal plates and fixed round the edges with Apiezon sealing compound. This arrangement was satisfactorily gas-tight, and enabled the windows to be removed easily at intervals for cleaning. All varnish was removed from the rock salt prism and end plates before use, since preliminary measurements indicated the disturbing influence of varnish absorption bands. A copious and frequently renewed supply of calcium chloride placed within the box of the instrument protected the rock salt prism adequately. The two absorption cells were placed parallel to each other in a rocking device by means of which each cell could in turn be brought into the line of the beam before the entrance slit. The galvanometer was of the moving magnet type and was enclosed in a mu metal shield. It was mounted on a solid stone support, and apart from exceptional circumstances, maintained a satisfactorily steady zero. Amplification was not employed. The slit widths were so adjusted that except for a small region at the extreme long wave-lengths, the throws through the blank cell exceeded 10 cm . on a scale viewed through an eye-piece before the galvanometer mirror and set up about I metre from the latter. The zero error did not as a rule exceed 0.5 mm . In taking readings the galvanometer throws were measured.

The dimethyl zinc was a commercial product purified by

TABLE 1.

| Wave-length $(\mu)$. | Frequency <br> $(\mathrm{cm} .-1)$. | Intensity. |
| :---: | :---: | :---: |
|  |  |  |
| 16.2 | 617 | v. strong |
| 14.2 | 704 | v. strong |
| 8.48 | 1180 | strong |
| 7.66 | 1305 | medium |
| 7.4 I | 1350 | med. weak |
| 6.92 | 1445 | v. weak |
| 6.49 | 1541 | v. weak |
| 5.91 | 1692 | medium |
| 5.59 | 1789 | med. weak |
| 5.3 | 1887 | v. weak |
| 4.75 | 2105 | v. weak |
| 3.42 | $(2924)$ | v. strong |
| 2.9 | 3450 | strong |
| 2.4 | 4167 | weak |
| 2.28 | 4386 | medium |
| 1.73 | 5781 | weak |
|  |  |  |
|  |  |  |
|  |  |  | distillation in vacuo. The vapour pressure and purity of the sample were previously measured by Thompson and Limett. ${ }^{8}$

## Results.

The pressures of vapour used varied from $7-200 \mathrm{~mm}$. The transmission curves between $1-17 \mu$ are shown in Fig. 1 , and in Table I are listed the maxima of the bands observed.

The slit widths used in the various regions are indicated in the diagram. None of the bands revealed contour. The band at $14.2 \mu$ was extremely intense and the region of absorption around $3.4 \mu$ could not be resolved, although some suggestions of structure were noticed.

## Discussion.

The Raman measurements of Venkateswaran and Pai with the liquid are in good agreement and lead to the following Raman frequencies: 144 (weak), 248 (v. weak), 488 (weak), 505 (strong), 620 (medium), 1160 (strong), 1346 (v. weak), 1443 ? (extremely weak), 2890 (strong).

[^2]The two lowest frequencies I44 and 248 found by Pai have analogues of approximately the same magnitude in the related molecules mercury


Fig. I.-The pressures used were: I. $12 \mathrm{~mm} . ; 2.7 \mathrm{~mm} ; 3.40 \mathrm{~mm}$; 4. 200 mm . ; 5.20 mm .


Fig. 2.
dimethyl, zinc and mercury diethyl. The value 1443 is somewhat doubtful. It could not be detected by Pai.

Before attempting to correlate the infra-red and Raman frequencies it is necessary to consider the plausible symmetry forms of the molecule. Various physical measurements such as those of dipole moment and crystal structure ${ }^{9}$ suggest that the $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ skeleton is linear but easily deformable. If this is so, three possible structures (Fig. 2) may be written, (i) the eclipsed form $\mathrm{D}_{3 h}$, (ii) the "staggered" form $\mathrm{D}_{3 d}$ (internal rotation from the eclipsed through $60^{\circ}$ ), and (iii) a structure in which rotation of the methyl groups about the $\mathrm{Zn}-\mathrm{C}$ bonds is unrestricted. If the $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ chain is not linear, the highest degree of symmetry obtainable corresponds to $\mathrm{C}_{2 v}$. It will be most convenient

[^3]to examine in turn how satisfactorily each of these models agrees with the measurements.

1. The form $D_{3 h}$ has a threcfold rotation axis $C_{3}{ }^{z}$, four planes of symmetry $\sigma_{z}$ and $3 \sigma_{x}$, and three equivalent twofold rotation axes $\mathrm{C}_{\psi}$. There will be seven single and seven twofold degenerate vibrations. The vibration types, their symmetry properties, and the selection rules and polarisation for the Raman and infra-red spectra are summarised in Table II.

According to Table II there will be ten permitted Raman frequencies and seven allowed fundamentals in the infra-red, with four frequencies possible in both. One vibration-the torsional oscillation-will be forbidden as a fundamental both in the Raman and in the infra-red.

If we disregard the doubtful Raman interval of 1443 , there are two satisfactory coincidences between the two sets of frequencies, namely

TABLE II.*

| Type. | Symmetry with respect to |  |  |  | Allowed in |  | Total. |  | Form. | $\begin{aligned} & \text { Value } \\ & \text { Assumed. } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $c_{3}{ }^{\text {a }}$. | $\sigma_{x}$. | $\sigma_{x}$. | $c_{\text {r }}$ | Raman. | I. Red. |  |  |  |  |
| $\mathrm{A}_{1}{ }^{\prime}$ | $s$ | $s$ | $s$ | $s$ | Yes (P) | No | 3 | $\nu_{1}$ $\nu_{3}$ $\nu_{3}$ | $\mathrm{CH}_{3}$ valency <br> $\mathrm{CH}_{3}$ deformation <br> $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ valency | $\begin{array}{r} 2890 \\ 1160 \\ 505 \end{array}$ |
| $\mathrm{A}_{1}{ }^{\prime \prime}$ | $s$ | as | as | $s$ | No | No | 1 | $\nu_{4}$ | torsional | $\sim 130$ |
| $\mathrm{A}_{2}{ }^{\prime \prime}$ | $s$ | $s$ | as | as | No | Yes | 3 | $\begin{aligned} & \nu_{5} \\ & \nu_{8} \\ & \nu_{7} \end{aligned}$ | $\mathrm{CH}_{3}$ valency $\mathrm{CH}_{3}$ deformation $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ valency | $\begin{array}{r} 2900 \\ \quad 1180 \\ 704 \end{array}$ |
| $E^{\prime}$ | $e$ | $e$ | $s$ | $\varepsilon$ | Yes | Yes | 4 | $\begin{aligned} & \nu_{8} \\ & \nu_{9} \\ & \nu_{10} \\ & \nu_{11} \end{aligned}$ | $\mathrm{CH}_{3}$ valency $\mathrm{CH}_{3}$ deformation $\mathrm{CH}_{3}$ rocking $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ deformation | $\begin{array}{r} \sim 3000 \\ 1350 \\ 617 \\ \\ 144 \end{array}$ |
| E" | $e$ | $e$ | as | e | Yes | No | 3 | $\begin{aligned} & \nu_{12} \\ & v_{13} \\ & \nu_{16} \end{aligned}$ | $\mathrm{CH}_{3}$ valency $\mathrm{CH}_{3}$ deformation $\mathrm{CH}_{3}$ rocking |  |

$620 / 617$ and $1346 / 1350$. Two magnitudes of 617 and 1350 would then fall in the $E^{\prime}$ group of four. Two vibrations of this group may be tentatively assigned in another way. First, $\nu_{8}$, the $\mathrm{E}^{\prime}$ methyl valency vibration will be about 3000 , and secondly, the deformation frequency $\nu_{11}$ of the $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ chain will be expected to be very small. From a comparison of the magnitudes of the deformation frequencies in related molecules it would seem correct to assign the Raman interval I44 to $\nu_{11}$ - The deformation vibration of the methyl group in ethane has a magnitude 1465; 1350 can therefore be assigned to $\nu_{9}$, and hence $\nu_{10}=617$; $\nu_{11}$ would naturally not be included in the infra-red region at present examined. The intense absorption of $\nu_{10}$ is paralleled by the intense absorption of the rocking frequency of ethane.

It seems unlikely that any fundamental other than the $\mathrm{CH}_{3}$ valency vibration can exceed $1500 \mathrm{~cm} .^{-1}$ in magnitude. On this basis there

[^4]remain four Raman frequencies which are not found in the infra-red, $248,488,505$, and II 60 , but the first three lie beyond the range of our measurements ; 505 is intense, and is almost certainly to be interpreted as $\nu_{3}$, the symmetrical vibration of the $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ chain; 1160 is also intense, and is a reasonable value for $\nu_{2}$, the $\mathrm{A}_{1}^{\prime}$ class methyl group deformation; $\nu_{1}$ can be identified with the interval 2890.

Class $\mathrm{A}_{2}{ }^{\prime \prime}$ involves vibrations permitted only in the infra-red. We should expect $\nu_{7}$ to be rather greater than $\nu_{3}$, and $\nu_{8}$ similarly somewhat greater than $\nu_{2}$. We may therefore write $\nu_{7}=704$ (the intense infrared band) and $\nu_{6}=1180 ; \nu_{5}$ will be close to 2900.

There remains unassigned the torsional oscillation in $\mathrm{A}_{1}{ }^{\prime \prime}$, and three Raman active vibrations in class $\mathrm{E}^{\prime \prime}$. The remaining Raman intervals, 248 and 488 , are each far too small to belong to class $\mathrm{E}^{\prime \prime}$, and some other interpretation must be found for them. It has been mentioned above that the interval of about 250 appears with the other related metal alkyls. This suggests that, despite its low intensity, it is real. The most plausible explanation of its occurrence is to regard it as the harmonic of $\nu_{4}$, which in contrast with the fundamental $A_{1}^{\prime \prime}$ will have the symmetry

TABLE III.

| Wave Number. | Interpretation. | Class. | $\nu$ calc. |
| :---: | :---: | :---: | :---: |
| 1305 | $\nu_{2}+\nu_{11}$ | E' | 1304 |
| 1445 | $\nu_{2}+2 \nu_{11}$ | E' | 1448 |
| 1541 | $2 \nu_{7}+\nu_{11}$ | $\mathrm{E}^{\prime}$ | 1552 |
| 1692 | $\nu_{8}+\nu_{3}$ | $\mathrm{A}_{2}{ }^{\prime \prime}$ | 1685 |
| 1789 | $\nu_{2}+\nu_{10}$ | $\mathrm{E}^{\prime \prime}$ | 1780 |
| 1887 2105 | $\stackrel{\text { ? }}{3}$ | $\widehat{A}^{\prime \prime}$ | 2112 |
| 2924 | $\nu_{58} \nu_{8}$ | $\mathrm{A}_{2}{ }^{\prime \prime} \mathrm{E}^{\prime \prime}$ | $\sim 3000$ |
| 3450 | $\nu_{8}+\nu_{3}$ | ${ }^{\text {A }}{ }^{\prime}{ }^{\prime}$ | $\sim 3505$ |
| 4167 | $\left\{\nu_{8}+\nu_{3}\right.$ | $\mathrm{E}^{\prime}$ | $\sim$ |
| 4188 | $\left\{\begin{array}{l}\nu_{12}+\nu_{0} \\ 3\end{array}\right.$ | $\mathrm{E}^{\prime}$ | $\sim 4180$ |
| $\begin{aligned} & 4386 \\ & 578 \mathrm{I} \end{aligned}$ | $\begin{aligned} & ? \nu_{12}+\nu_{13} \\ & v_{1}+\nu_{5} \end{aligned}$ | ${ }_{\text {E }} \mathrm{E}^{\prime \prime}$ | $\begin{array}{r} \sim_{4375} \\ \sim \\ \sim \end{array}$ |

$\mathrm{A}_{1}^{\prime}$ and be Raman-active ( $s, a s, a s$, $s \times s, a s, a s, s=s, s, s, s)$. Making a small allowance for the anharmonicity, we should then write $\nu_{4} \sim$ I30. The Raman interval 488 is then best explained as $(620-130)=490$.

In class $E^{\prime \prime}$ we can write $\nu_{12} \sim 3000 ; \nu_{13}$ and $\nu_{14}$ are not apparently observed; $\nu_{13}$ would be expected to have a magnitude about 1350-1400. It is, of course, possible that $\nu_{g}$ is not really observed in the Raman spectrum, and that the interval 1346 should be attributed to $\nu_{13}$. The value of $\nu_{14}$ cannot be predicted with much accuracy, but it ought to lie within the range 700-1 100, and the only hope of assessing its magnitude is by a study of the combination bands.

In Table III the infra-red bands not accounted for above are given, with possible interpretations. Except for the band at $1887 \mathrm{~cm} .^{-1}$ (very weak), for which there does not appear to be a suitable combination of observed frequencies, the interpretations are satisfactory. This band could be attributed cither to the overtone of the missing fundamental, $\nu_{1 s}$, or to a combination of this fundamental with some other frequency. A decision between these alternatives cannot be made. If the band is the overtone, $\nu_{14}$ will have a value of about 950 .
2. The staggered form $\mathrm{D}_{34}$ has a threcfold rotation axis $\left(\mathrm{C}_{3}{ }^{z}\right)$, three equivalent twofold rotation axes $\left(C_{y}\right)$, three equivalent planes of symmetry $\sigma_{\nu}$ and a centre of symmetry $i$. There will, again, be seven single and seven twofold degenerate vibrations. The types, numbers, and form of these vibrations are given in Table IV.

Important inferences of Table IV are that there should be no "coincidences" in the Raman and infra-red, that six frequencies are permitted in the Raman spectrum and seven in the infra-red. As
before, the torsional vibration $\nu_{4}$ will be forbidden as a fundamental both in the Raman spectrum and in the infra-red.

As already seen, at least two apparent coincidences are found, namely $617 / 620$ and I346/I 350 , and in addition there may be one at 2890 and others below $600 \mathrm{~cm} .^{-1}$ in the unexamined infra-red region. These coincidences might be explained in one of two ways; either the molecule is highly flexible, so that in the liquid state selection rules break down and unexpected Raman frequencies appear; or on the other hand the coincidences may be accidental and arise from fortuitous agreement between the magnitudes of certain frequencies. The latter hypothesis is unlikely, although in a molecule of this kind, in which the two methyl groups tend to preserve their individuality and are subject to only slight interactions, such close groupings are possible. It might explain the coincidence 1346/1350, but is less likely to account for that at $617 / 620$. The former hypothesis needs more careful consideration.

TABLE IV.

| Type. | Symmetry with respect to |  |  |  | Allowed in |  | Total. |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $C_{3}{ }^{2}$. | $C_{r}$ | $\sigma$. | $i$. | Raman. | I. Red. |  |  | Form, |
| $\mathrm{A}_{10}$ | $s$ | $s$ | 5 | $s$ | Yes (P) | No | 3 | $\nu_{1}$ $\nu_{2}$ $\nu_{3}$ | $\mathrm{CH}_{3}$ valency $\mathrm{CH}_{3}$ deformation $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ valency |
| $\mathrm{A}_{1 u}$ | $s$ | $s$ | as | as | No | No | 1 | $\nu_{1}$ | torsional |
| $\mathrm{A}_{2 u}$ | $s$ | as | $s$ | as | No | Yes | 3 | $\nu_{5}$ $\nu_{6}$ $\nu_{7}$ | $\mathrm{CH}_{3}$ valency <br> $\mathrm{CH}_{3}$ deformation <br> $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ valency |
| E | $e$ | $e$ | $e$ | $s$ | Yes | No | 3 | $v_{8}$ $\nu_{9}$ $v_{10}$ | $\mathrm{CH}_{3}$ valency $\mathrm{CH}_{3}$ deformation $\mathrm{CH}_{3}$ rocking |
| $\mathrm{E}_{u}$ | $e$ | $e$ | $\varepsilon$ | as | No | Yes | 4 | $\nu_{11}$ $\nu_{12}$ $\nu_{13}$ $\nu_{14}$ | $\mathrm{CH}_{3}$ valency <br> $\mathrm{CH}_{3}$ deformation <br> $\mathrm{CH}_{3}$ rocking <br> $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ deformation |

As for the symmetry $\mathrm{D}_{3 h}, 505,2890$, and 1160 can be assigned to $\nu_{3}, \nu_{1}$, and $\nu_{2}$, and similarly $\nu_{7}, \nu_{6}$, and $\nu_{5}$ can be given the values 704 , I180, and 2900; $\nu_{8}$ and $\nu_{11}$ will have a value $\sim 3000 ; \nu_{9}$ and $\nu_{12}$ can be conveniently associated with I 346 (Raman) and I350 (infra-red). The values of four frequencies now remain unfixed, namely $\nu_{4}, \nu_{10}, \nu_{13}, \nu_{14}$. The unassigned Raman frequencies are 144, 248, 488, 620 , and the outstanding plausible infra-red fundamentals are 617,$1305 ; \nu_{4}$ can again be taken as $\sim 130$, the harmonic giving the Raman interval 248. The most reasonable assumption is now to take $\nu_{14}=144, \nu_{10}=617$, and $\nu_{13}=620$, and explain the Raman interval 488 as before

$$
(620-130=490)
$$

This interpretation involves the breaking of the selection rules for $v_{14}$ in the Raman spectrum of the liquid. If ease of distortion leading to the symmetry $D_{3 \hbar}$ is the cause of this, we might expect such a state of
affairs to be effectively equivalent to a state of unrestricted internal rotation. Again, it is rather improbable that $\nu_{10}$ and $\nu_{13}$ really lie as close together as this assignment suggests. Here, too, we could invoke a failure of the Raman selection rule and attribute both 617 and 620 to $\nu_{13}$, but this is an additional ad hoc argument. Further difficulties are found, however, in the interpretation of the overtones and combinations. For example, 1305 and 1445 cannot be described by the same numerical combinations as for the $\mathrm{D}_{3 h}$ form, and although a satisfactory explanation can be found for $1692(1180+505), 1789(1160+620)$ and 2105 ( $3 \times 704$ ), and possibly $1305(704+617$ ), there will be three unexplicable infra-red values, namely 1445, 1541, and 1887. It might be possible, as discussed for the $\mathrm{D}_{3 h}$ form to attempt with a modified assignment to introduce an additional unobserved fundamental to account for these, but according to the present assignment no normal mode remains to which such a frequency could be attached.

Taken as a whole, therefore, the facts appear to be in less satisfactory agreement with the symmetry $\mathrm{D}_{3 d}$ than with $\mathrm{D}_{3 h}$.
3. The third possible structure is the non-linear form, the highest symmetry of which will be $\mathrm{C}_{2 v}$, involving a twofold axis of rotation $\mathrm{C}_{2}{ }^{z}$ and two planes of symmetry $\sigma_{x}$ and $\sigma_{y}$. The normal modes fall into four groups:
$\mathrm{A}_{1}$. Seven frequencies. Raman ( P ) and infra-red active. (Two $\mathrm{CH}_{3}$ valency vibrations; $\mathrm{CH}_{3}$ deformation; $\mathrm{CH}_{3}$ bending; $\mathrm{CH}_{3}$ rocking; $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ valency; $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ deformation.)
$\mathrm{A}_{2}$. Four frequencies. Raman active. $\left(\mathrm{CH}_{3}\right.$ valency vibration; $\mathrm{CH}_{3}$ bending ; $\mathrm{CH}_{3}$ rocking ; torsional.)
$\mathrm{B}_{1}$. Four frequencies. Raman and infra-red active. $\left(\mathrm{CH}_{3}\right.$ valency vibration; $\mathrm{CH}_{3}$ bending; $\mathrm{CH}_{3}$ rocking; torsional.)
$\mathrm{B}_{2}$. Six frequencies. Raman and infra-red active. (Two $\mathrm{CH}_{3}$ valency vibrations; $\mathrm{CH}_{3}$ deformation; $\mathrm{CH}_{3}$ bending; $\mathrm{CH}_{3}$ rocking; $\mathrm{C}-\mathrm{Zn}-\mathrm{C}$ valency.)
It is seen that twenty-one frequencies are possible in the Raman spectrum and seventeen as fundamentals in the infra-red. Seventeen coincidences are therefore permitted. Excluding the high $\mathrm{CH}_{3}$ valency vibrations there will be cleven coincidences. Actually, below $1500 \mathrm{~cm} .^{-1}$, only three possible coincidences are observed ( $620 / 617,1346 / 1350$ ) and possibly $1160 / 1180$ ), although it is possible that two others below 600 may lie in the inaccessible infra-red region. Hence the facts are more in favour of some other molecular symmetry. Moreover, of the four lowest Raman frequencies observed it is unlikely that two, and at the most three, can be fundamentals. In this case at least five, probably six, and perhaps more than six, frequencies fail to appear in either the Raman spectrum or infra-red. It would be possible to assign the observed numerical magnitudes to different normal modes, but any such assignment is very ambiguous and incomplete, and as a whole the facts again suggest that the $\mathrm{C}_{2 v}$ structure is less satisfactory than either of those discussed above.

To summarise, therefore, while no certain conclusions can be drawn, the eclipsed linear structure $D_{3 h}$ seems the most probable. The interpretation suggested for the low frequencies appears more reasonable than any other alternative. In particular, if the Raman interval is correctly identified with the torsional frequency it implies that internal rotation is restricted, but the molecule is not very rigid towards the torsion. No quantitative estimate can be made of the potential barrier,
but it may not be very high. Specific heat data would be valuable in testing these conclusions.

## Summary.

The infra-red spectrum of dimethyl zinc has been studied between I-I7 $\mu$, and the data have been correlated with known Raman data. Assignment of the various frequencies to normal modes has been examined for different possible classes of molecular symmetry. Some ambiguity remains, but the facts suggest that the molecule has the linear structure $\mathrm{D}_{3}$, but may be flexible. In the normal state there appears to be a torsional oscillation indicating restricted internal rotation, but the potential barrier between this state and that of free rotation may be small.

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## THE INFRA-RED AND RAMAN SPECTRA OF ETHYLENE SULPHIDE.

By H. W. Thompson and D. J. Dupré.<br>Received 14th May, 1940.

The only observations on the spectrum of ethylene sulphide appear to be those of Eyster, ${ }^{1}$ who measured several absorption bands in the photographic infra-red. Although an asymmetrical rotator, the molecule in all probability falls in the symmetry group $\mathrm{C}_{2 v}$ and possesses several elements of symmetry. The application of selection rules and similar considerations to Raman and infra-red data may therefore throw some light on the normal vibration frequencies of the molecule. Being fairly volatile, the substance is experimentally suitable for such infra-red measurements, which are the more desirable since few simple molecules of any degree of symmetry remain unexamined. Moreover, ethylene sulphide provides an example of an asymmetric rotator, the contour of whose vibration bands may serve to confirm predictions made by Badger and Zumwalt ${ }^{2}$ for such molecules and not yet adequately tested. Some of the photographic infra-red bands observed by Eyster revealed an interesting contour.

In the present work the absorption spectrum has been studied over the range $\mathrm{I}-17 \mu$, and the Raman spectrum has been measured. The infra-red and Raman spectra of the related molecule ethylene oxide have been described by several workers, notably by Eyster ${ }^{1}$ and by Linnett. ${ }^{3}$

## Experimental.

The infra-red spectrometer was the large aperture Hilger instrument D 88, with interchangeable prisms of fluorite, rock salt, sylvine and quartz, suitably modified so as to incorporate a vacuum thermocouple. The wave-

[^5]length drum was repeatedly checked against known bands. The details of the whole arrangement have been described previously. ${ }^{\text {a }}$ The absorption cells were as a rule glass tubes 2.5 cm . in diameter and 21 cm . in length, with square rock salt end plates sealed on in the manner indicated previously. The source of radiation was an electrically heated Globar rod.

For the measurement of the Raman spectrum a glass prism spectrograph of very high aperture and resolving power was used. The exciting lines were taken from a 500 candle-power mercury arc, with suitable filters. The arrangement was essentially that of Wood, in which a cylindrical glass tube, 5 cm . in diameter and 20 cm . in length, containing a filter solution and simultaneously acting as a cylindrical condenser, was placed before the mercury arc with its axis parallel to the Raman tube and to the axis of the spectrograph. The Raman tube, a cylindrical pyrex tube of 30 c.c. capacity with outer water condenser and with metal reflector all along its length, was placed with its rounded end before the slit of the spectrograph. A solution of copper ammonium sulphate was used as filter. This transmitted the lines 4358 A . and 4047 A ., and to a much less extent that at 3650 A. Raman displacements were observed from each of these exciting lines. Slight polymerisation of the ethylene sulphide, however, appeared to be responsible for an unavoidable background scattering. In order to

TABLE $I$.

| Interval $\mathrm{cm}^{-1}$. | Exciting Lines. | Intensity. | Polarisation. |
| :---: | :---: | :---: | :---: |
| 625 | $k, e$ | strong | polarised |
| 660 | $k, e$ | weak |  |
| 827 | $k$ | weak | - |
| $94^{1}$ | k, e | very weak |  |
| 1040 | $k, e$ | medium | polarised |
| 1120 | $k, e$ | strong | polarised |
| 1450 | $e$ | very weak | polarised ? |
| 2890 | $k_{\text {, }}$ e | very weak |  |
| 2990 | $k, e, q$ | strong | polarised |
| 3085 | $k, e, q$ | medium | - | minimise this polymerisation, the shorter wave-lengths were eliminated as much as possible. For this purpose an additional filter of a dilute solution of nitrobenzene in ethyl alcohol was used in conjunction with the previous filter. This combination transmitted the line at 4358 A . but cut off all shorter wavelengths, and this procedure was of additional advantage in correlating the observed Raman displacements with the different exciting frequencies. Satisfactory exposures could be obtained in 6-12 hours.

The polarisation of the Raman lines was examined, using polaroid. The latter was placed between the mercury arc and Raman tube and two independent exposures made with the polaroid successively transmitting the component vibrating parallel or perpendicular to the Raman tube. When used in this manner, the polaroid (one of a pair of spectacle glasses) became gradually photolysed by stray ultraviolet light, probably 3650 A. In later experiments it was placed before the slit of the spectrograph, two exposures being made, with the polaroid transmitting in a plane either parallel or perpendicular to the slit. This method is rather less satisfactory than the former. A superposed copper arc was used for the determination of wave-lengths. Ilford special rapid panchromatic and Wellington antiscreen plates were used.

The ultraviolet absorption of ethylene sulphide was also examined over the range 2000-4000 A., using a Hilger E 315 quartz instrument.

For the preparation of ethylene sulphide the method of Delèpine and Eschenbrenner ${ }^{5}$ was used. Ethylene dithiocyanate was first obtained by heating ethylene dibromide with potassium thiocyanate in alcohol under a reflux for four hours. The product was crystallised from aqueous solution. A mixed solution of sodium sulphide and sodium hydrogen sulphide was

[^6]${ }^{5}$ Bull. Soc. Chim., 1923, 33, 703.
then slowly added in the cold with stirring to the solid ethylene dithiocyanate. After prolonged shaking the mixture was steam distilled, and the first portion of the distillate was nearly pure ethylene sulphide. This product was dried with calcium chloride and redistilled, and boiled at $55^{\circ} \mathrm{C}$. While some of the specimens prepared remained unchanged for many weeks, others polymerised rapidly. The precise factors determining this polymerisation could not be ascertained, but the solution of the sulphides must be prepared with care by saturating caustic soda solution with hydrogen sulphide and then adding the calculated quantity of caustic soda.

Owing to the polymerisation it was necessary to clean the absorption cells repeatedly.

## Results.

(a) The Raman Spectrum.-Table I summarises the mean Raman displacements deduced. In this table, $k, e$, and $q$ denote the exciting lines 4047 A., 4358 A., and 3650 A.


Fig. 1.-The pressures used were : 1. 80 mm .; 2. 100 mm . ; 3. 250 mm . 4. $150 \mathrm{~mm} . ; 5.60 \mathrm{~mm} . ; 6.30 \mathrm{~mm} . ; 7.10 \mathrm{~mm}$. and 8. 200 mm .
(b) The Infra-Red Spectrum.-Fig. I shows the transmission curve for various pressures of vapour between $580-7000 \mathrm{~cm} .^{-1}$. The slit widths used are indicated. It is seen that although the maximum vapour pressure available (c. 250 mm .) brought out most of the bands sufficiently strongly, a few bands were still very weak; but even if a higher pressure could have been used these feeble bands would have become submerged in the more intense bands.

## Discussion.

The ethylene sulphide molecule probably belongs to the symmetry group $\mathrm{C}_{2 v}$. There is a twofold rotation axis ( $z z$ in Fig. 2) and two planes
of symmetry $\sigma_{x}$ and $\sigma_{y}$. There will be fifteen normal vibrations. The selection rules and division of these vibrations into symmetry classes are given in Table II.
It is seen that all fifteen frequencies are permitted to appear in the Raman effect, and five should be polarised. Three frequencies are forbidden in the infra-red, the remaining twelve falling into three groups in which the change in electric moment is parallel to the $z$ axis $\left(\mathrm{M}_{z}\right)$ or to the $x$ or $y$ axis.

It is worth considering whether the rotational contour of bands observed in the infra-red can be used as a guide in the allocation of the different vibration frequencies to the different symmetry classes. The molecule is asymmetric, and according to Eyster (loc. cii.) we may take as approximate moments of inertia $\mathrm{A} \sim 38.8, \mathrm{~B} \sim 74.8$ and $\mathrm{C} \sim 102 \times 10^{-40} \mathrm{gm} . \mathrm{cm} .^{2}$ Badger and Zumwalt $^{6}$ have discussed the theoretical contours of vibration bands for molecules of varying degrees of asymmetry. They have conveniently designated three types of rotational structure A, B and C according as the change in



Deformation


Rocking


Bending


Twisting


Fig. 3.

Fig. 2.
electric moment is parallel to the least, intermediate, or major axis of inertia. With ethylene sulphide the $A_{1}$ symmetry class vibrations will give rise to A type contours; the $\mathrm{B}_{1}$ class vibrations will give $B$ type contours, and the $B_{2}$ class will give $C$ type contours. Assuming the above moments of inertia and the nomenclature of Badger and Zumwalt $\rho=1 \cdot 19$ and $S=-\cdot 55$. The general form of the A, B, and C types to be expected are shown in Fig. 3 (full lines). Eyster has shown diagrammatically a measured band of the B type found at $8775 \mathrm{~cm} .^{-1}$ and states that the A and C type bands also found have the predicted forms. The difference in contour might indeed therefore suggest a valuable guide in the identification of the normal modes. Unfortunately the comparatively low resolving power used in the present measurements complicates the problem. From the formulæ of Badger and Zumwalt the approximate spacings between the maxima in each of the several band types can be estimated. It is found that the two central peaks in the B type band of ethylene sulphide should be separated by about $I 3 \mathrm{~cm} .^{-1}$, which is in satisfactory agreement with the band observed by Eyster. In this case it is unlikely that even with the
smallest slit widths used in the present work the two peaks would be resolved, and we might expect the contours to follow roughly the dotted curves. In the same way the separation of the extreme maxima ( $P$ and $R$ ) in the A type band should lie about $24 \mathrm{~cm} .^{-1}$ apart. These maxima may be separable in the present work in some regions of the spectrum, but it is hardly likely that the central Q branch will be distinguished, and the contour will probably appear as the dotted curve with two maxima. In the same way the C type band will be affected by the smaller resolving power, but not fundamentally altered in appearance, and although now similar to the type $B$ contour, should be distinguishable from the latter by its sharper and rather more intense Q branch.

We are now in a position to attempt an assignment of the various frequencies. Of the Raman lines, five are polarised, namely 625, 1040, II 20, I450 and 2990. The rules given in Table II therefore suggest that this array of frequencies represents the group $A_{1} ; 2990$ can clearly be

TABLE 11.

| Symmetry | Syrmmetry with respect to |  |  | Permitted in |  | Total. |  | Form. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Type. | $C_{2}{ }^{\text {a }}$. | $\sigma_{x}$. | $\sigma_{v}$ | Raman. | Infra-Red. |  |  |  |
| $\mathrm{A}_{1}$ | $s$ | $s$ | $s$ | Yes (P) | Yes ( $\mathrm{Ma}_{3}$ ) | 5 | $\nu_{1}$ | CH valency |
|  |  |  |  |  |  |  | $\nu_{2}$ | $\mathrm{CH}_{2}$ deformation |
|  |  |  |  |  |  |  | $\nu_{3}$ | $\mathrm{CH}_{2}$ bending |
|  |  |  |  |  |  |  | $\nu_{3}$ | ring deformation |
| $\mathrm{A}_{2}$ | $s$ | as | as | Yes | No | 3 | $v_{6}$ | CH valency |
|  |  |  |  |  |  |  | $\nu_{7}$ | $\mathrm{CH}_{2}$ rocking |
|  |  |  |  |  |  |  | $\nu_{8}$ | $\mathrm{CH}_{2}$ twisting |
| $\mathrm{B}_{1}$ | as | as | $s$ | Yes | Yes ( $\mathrm{M}_{x}$ ) | 4 | $\nu_{9}$ | CH valency |
|  |  |  |  |  |  |  | $\nu_{10}$ | $\mathrm{CH}_{2}$ deformation |
|  |  |  |  |  |  |  | $v_{11}$ | $\mathrm{CH}_{2}$ bending |
|  |  |  |  |  |  |  | $\nu_{12}$ | ring deformation |
| $\mathrm{B}_{2}$ | as | $s$ | as | Yes | Yes ( $\mathrm{M}_{v}$ ) | 3 |  | CH valency |
| $\mathrm{B}_{2}$ |  |  |  |  |  |  | $\nu_{14}$ | $\mathrm{CH}_{2}$ rocking |
|  |  |  |  |  |  |  | $\nu_{15}$ | $\mathrm{CH}_{2}$ twisting |

assigned to $\nu_{1}$ the CH valency vibration, and 1450 to $\nu_{2}$ the deformation vibration of the methylene group. The two lowest frequencies 625 and 1040 may be reserved for the ring deformations $\nu_{5}$ and $\nu_{4}$ respectively, leaving $\nu_{3}=1120$. All these frequencies are permitted in the infra-red; actually only four are found. At 625 there is a band with a double branch appearance suggesting in the present case an A type band and therefore agreeing with the assignment of $\nu_{5}$. Moreover, the separation of the branches is about $22 \mathrm{~cm} .^{-1}$, close to the value to be expected. At 1042, agreeing with $\nu_{4}$ is a very intense band showing traces of structure, at the peak, but since the resolving power in this region is small, complete resolution is hardly to be expected. A similar unresolved band appears at I44I agreeing with $\nu_{2}$. The intense region of absorption at $3 \cdot 3 \mu$ has not been resolved, but may well contain a band at 2990. The inzo frequency attributed to $\nu_{3}$ does not appear in the infra-red. It is associated with the simultaneous symmetrical bending of the two methylene groups, and was not observed in the spectrum of ethylene oxide, although
in the latter case there was the possibility of its being masked by another band. The value 1040 assigned to the ring deformation $\nu_{4}$ is also very plausible, since for a vibration largely determined by the vibration of the $\mathrm{C}-\mathrm{C}$ bond a value of about 1000 would be expected, and might be expected to be intense in the infra-red.

The unidentified Raman intervals are 660, 827, 941, 2890 and 3085. It is probable as with many other methyl compounds that 2890 is the overtone of $\nu_{2}(2 \times 1450=2900)$; and 3085 can be attributed to the CH valency vibrations ( $\nu_{6}, \nu_{13}$ ) of either the $\mathrm{A}_{2}$ or $\mathrm{B}_{2}$ class, since these frequencies will have roughly the same value and be somewhat higher than $\nu_{1}$ and $\nu_{\mathrm{g}}$. Here again this frequency may be submerged in the infra-red absorption around $3.3 \mu$. Of the other three Raman values, 941 and 827 appear in the infra-red at 949 (strong) and 823 (weak). Whatever the nature of these vibrations, they cannot by the selection rules belong to the $A_{2}$ group. The contour of the infra-red band at 949, however, has the appearance to be expected for a B type band, placing it in the class $\mathrm{B}_{1}$. It must therefore be assigned to one of $\nu_{10}$, $\nu_{11}$, and $\nu_{12}$. Now, of the three ring deformations, one (1040) will largely involve a vibration of the $\mathrm{C}-\mathrm{C}$ bond; the other two will represent symmetric and antisymmetric oscillations involving mainly the $\mathrm{C}-\mathrm{S}$ bonds. The symmetric vibration was taken to be $625 ; \nu_{12}$ should be somewhat, though not considerably, greater than this. The antisymmetric $\mathrm{CH}_{2}$ deformation, $\nu_{10}$, will have a value not very different from 1445. It is clear, therefore, that we can write $\nu_{11}=949$ (infra-red) corresponding to the Raman value of 941 .

The remaining unidentified Raman frequencies are now 660 and 827. The former frequency is not observed in the infra-red. Around 700 $\mathrm{cm} .^{-1}$ there is a complex absorption at first suggestive of a single well resolved B type contour, but since the two maxima are $25 \mathrm{~cm} .^{-1}$ apart this cannot be correct. Bands are therefore suggested at 686 and 71 I. Moreover, the band at 7II has a similar contour to that at 949, and can therefore be assigned to $\nu_{12}$. It seems natural to assign 660 to $\nu_{8}$ in accordance with the selection rules. The alternative would be to assign 660 to $\nu_{7}$. In principle this is possible, but a consideration of the data with related molecules such as ethylene oxide and cyclopropane seem to make it unlikely ; $\nu_{8}$ involves a twisting of the methylene groups with respect to each other. The other twisting vibration, $\nu_{15}$, will have a value not far removed from that of $\nu_{8}$, and we can therefore write $\nu_{15}=686$. Of the two rocking vibrations, only $\nu_{14}$ will be permitted to appear in the infra-red, and may well explain the band at $823 \mathrm{~cm} .^{-1}$ and Raman interval 827.

Two frequencies, $\nu_{10}$ and $\nu_{\eta}$, remain unallocated. It is very probable that $\nu_{10}$ has a value close to that of $\nu_{2}$. It is possible that the feeble band at $c$. 1390 overlaid by the stronger band at I44I is due to $\nu_{10}$. The methylene rocking vibration $\nu_{7}$ should lie in the region $800 \cdot 1100 \mathrm{~cm} .^{-1}$, but the data so far given do not enable us to decide its precise value.

Table III summarises the above conclusions, and includes the corresponding frequencies of ethylene oxide adopted by Linnett. The combination bands and overtones observed in the infra-red are given in Table IV, with suggested interpretations. It will be seen that with one exception a satisfactory interpretation can be given for each observed band. The unexplained frequency lies at $c .4250 \mathrm{~cm} .^{-1}$. It might be possible to attribute it to the combination ( $2 \nu_{2}+\nu_{10}$ ) (predicted value 4280 ), but this does not seem likely. Another possibility is that
it arises from a combination of the unassigned frequency $\nu_{7}$ with either 2990 or $3080 ; \nu_{7}$ would then have the value 1260 or 1170 . Either value, particularly the latter, is plausible for the missing $\mathrm{CH}_{2}$ rocking vibration, but it would be unwise to use this single criterion for fixing $\nu_{7}$.

TABLE III.

|  |  | Raman. | Infra-red. | Adopted. | Cthylene |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $A_{1}$ | CH valency | 2990 | (2990) | 2990 | 3000 |
|  | $\mathrm{CH}_{3}$ deformation | 1450 | I44I | 1445 | 1494 |
|  | $\mathrm{CH}_{2}$ bending | 1120 | not observed | 1120 | 1122 |
|  | ring deformation | 1040 | 1042 | 1040 | 1270 |
|  | ring deformation |  | 625 | 625 | 811 |
| $\mathrm{A}_{2}$ | CH valency | 3080 | forbidden | 3080 | 3062 |
|  | $\mathrm{CH}_{2}$ rocking $\mathrm{CH}_{2}$ twisting | not observed 660 | forbidden forbidden | $\overline{660}$ | 807 |
| $\mathrm{B}_{1}$ | CH valency | 2990 | (2990) | 2990 | 3000 |
|  | $\mathrm{CH}_{2}$ deformation | not observed | 1390 | 1390 | 1453 |
|  | $\mathrm{CH}_{2}$ bending | 94 I | 949 | 949 | 1163 |
|  | ring deformation | not observed | 7 II | 7 II | 868 |
| $\mathrm{B}_{2}$ | CH valency | 3080 | (3080) | 3080 | 3062 |
|  | $\mathrm{CH}_{2}$ rocking | $827$ | 823 | 823 | ${ }_{1172}$ |
|  | $\mathrm{CH}_{2}$ twisting | not obscrved | 686 | 686 | 673 |

TABLE IV.

| Wave-length ( $\mu$ ). | Frequency. | Intensity. | Interpretation. | Class. | Calculated Frequency, |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 8.1 | 1235 | weak | ${ }^{2} \nu_{5}$ | $\mathrm{A}_{1}$ | 1250 |
| $7 \cdot 6$ | 1316 | very weak | $\nu_{s}+v_{1 s}$ | $\left(A_{1}+B_{2}\right)=B_{2}$ | I3II |
| $5 \cdot 8$ | ? 1724 | very weak | $\nu_{4}+\nu_{18}$ | $\left(A_{1}+B_{2}\right)=B_{2}$ | 1726 |
| $4 \cdot 85$ | 2062 | medium | $\nu_{2}+\nu_{5}$ | $\mathrm{A}_{1}$ | 2070 |
| 4.41 | 2270 | very weak | $\nu_{2}+\nu_{14}$ | $\left(A_{1}+B_{2}\right)=B_{2}$ | 2268 |
| 2.72 2.35 | 3676 4250 | medium very weak | $\nu_{1}+\nu_{\text {? }}$ | $\left(\mathrm{A}_{1}+\mathrm{B}_{2}\right)=\mathrm{B}_{2}$ | 3676 |
| 2.22 | 4505 | medium | $\nu_{9}+\nu_{1}$ | $\left(A_{2}+B_{2}\right)=B_{2}$ |  |
|  |  |  |  | $\left(A_{1}+A_{1}{ }^{2}-B_{1}\right.$ | 4525 5980 6070 |
| I. 67 | 5988 | medium | $\left\{\begin{array}{l}\left(\nu_{1}+\nu_{0}\right) \\ \left(\nu_{1}+\nu_{13}\right)\end{array}\right.$ | $\begin{aligned} & \left(A_{1}+B_{1}\right)=B_{1} \\ & \left(A_{1}+B_{2}\right)=B_{2} \end{aligned}$ | 6070 6070 |

It was shown above that the rotational contour of the band at $625 \mathrm{~cm} .^{-1}$ is consistent with the probable moments of inertia. The separation of the branch maxima of this band is susceptible, however, to the resolving power, and cannot be measured to a sufficient degree of accuracy to make the converse calculation of the moment of inertia justifiable.*
*The ultraviolet absorption of ethylene sulphide vapour was examined between $4000-2000 \mathrm{~A}$. Using pressure of vapour less than Imm . in an absorption cell 30 cm . in length a few broad bands were observed at wave-lengths shorter than 2123 A . The approximate wave-lengths of the first three bands are 2123 A ., 2096 A., and 2072 A. A feebler extremely broad band occurs at c. 2158 A. With the plates available it was not possible to follow the bands to shorter wavelengths. The results indicate an electronic level at $47,100 \mathrm{~cm}^{-1}$, but the data are insufficient to make trustworthy estimates of the vibration intervals possible. The band system is similar in region and appearance to those of similar alkyl sulphides. ${ }^{7}$
${ }^{7}$ Thompson and Linnett, Proc. Roy. Soc., A, 1936, 156, 120.

## Summary.

The infra-red absorption spectrum of ethylene sulphide has been measured between $\mathrm{r}-\mathrm{x} 7 \mu$. The Raman spectrum has also been measured. The two sets of data have been applied to the assignment of magnitudes to the normal modes of vibration, and a plausible assignment of i4 out of 15 vibrations has been made. The envelopes of some of the infra-red bands have been discussed. Some observations on the ultra-violet spectrum have been recorded.

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# THE INFRA-RED SPECTRUM OF METHYL MERCAPTAN. 

By H. W. Thompson and N. P. Skerrett.

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The present paper summarises measurements on the infra-red absorption spectrum of methyl mercaptan vapour over the range of wavelengths I-I $6 \mu$. The spectra of several mercaptans have previously been studied, over a limited spectral region, but no complete survey of the spectrum of methyl mercaptan appears to have been made, and the assignment of the molecular frequencies to the different possible normal modes is still incomplete. A knowledge of the normal frequencies, and the infra-red data as a whole, are of value for two reasons. On the one hand, the corresponding measurements have recently been made for the two related molecules methyl alcohol ${ }^{1}$ and methylamine, ${ }^{2}$ so that a comparison of the data would be very useful; and on the other, it is interesting to discover the extent to which internal rotation about the $\mathrm{C}-\mathrm{S}$ bond is restricted. Moreover, methyl mercaptan is a relatively small and only slightly asymmetric molecule, so that there is some hope of applying spectroscopic measurements to the study of the molecular structure. The present measurements are a preliminary to a more detailed study of certain bands using higher resolving power. Attempts to analyse bands in the photographic infra-red using a grating spectrograph ${ }^{3}$ failed owing to the feeble absorption.

The Raman spectrum of liquid methyl mercaptan has been measured by Venkateswaran ${ }^{4}$ and by Wagner. ${ }^{5}$ Their values are discussed below. Coblentz ${ }^{6}$ studies the infra-red absorption of liquid ethyl mercaptan but does not appear to have made corresponding measurements with the

[^7]methyl derivative. Bell, Ellis, ${ }^{8}$ and Williams, ${ }^{9}$ have each studicd the infra-red absorption of liquid mercaptans other than the methyl compound, with a view to correlating certain regions of absorption with the presence of the S-H link in an organic molecule. For our present purpose these measurements are not very relevant, but it may be noted that the present data fall into line with them as regards the characteristic region of absorption of the mercaptan link.

The spectrometer was the large aperture Hilger instrument D 88 having interchangeable prisms of quartz, fluorite, rock salt and sylvine. The details of the experimental arrangement have been described elsewhere. ${ }^{10}$ The absorption cells were 21 cm . in length and 3 cm . in diameter, with rock salt end plates fixed on with Apiezon sealing compound.

The methyl mercaptan first used was an Eastman Kodak product, but this was found to contain an appreciable amount of dissolved sulphur dioxide. Repeated fractionation in vacuo failed to remove the latter, as measurements of the ultraviolet absorption spectrum showed. The sample was therefore distilled slowly through an aqueous solution of baryta, which was renewed at intervals. The issuing vapour was dried with calcium chloride and frozen out in a liquid air trap. No trace of sulphur dioxide could be detected in this product either in the infra-red or ultraviolet spectra.

The pressures used in the absorption cell varied between $30-700 \mathrm{~mm}$., preliminary measurements with a higher pressure indicating the most satisfactory conditions for the detailed study of any individual band. Some of the absorption bands were still very weak using the highest pressures.

## Results and Discussion.

Fig. I shows the percentage transmission curves between $I \cdot 5 \mu$ and I $5 \mu$, for the different pressures. The effective slit widths are also shown. It will be seen that at $14 \mu$ it was possible to work with slits equivalent to about $10 \mathrm{~cm} .^{-1}$ An enlarged diagram of the region $6-8 \mu$ is shown in Fig. 2.

Although in reality methyl mercaptan is an asymmetrical molecule, it approaches very closely in structure to the symmetrical rotator methyl chloride. The latter molecule has six normal vibrations, three of which are twofold degenerate. The presence of the fourth hydrogen atom in methyl mercaptan, presumably off the $\mathrm{C}-\mathrm{S}$ axis, introducing the slight asymmetry, will be expected to remove the degeneracy of the methyl halide type. Accordingly we shall expect to find twelve normal modes of methyl mercaptan, among which will be three reasonably close pairs. The results of Borden and Barker ${ }^{1}$ with methyl alcohol show that in this analogous case the splitting of the degenerate frequencies caused by the asymmetry is slight, but appreciable. Inspection of their curves suggests that $\nu_{6}$ splits into two frequencies, 1340 and 1230 , and $\nu_{4}$ into a pair, 1477 and 1405 , the smaller frequency of the pair being the weaker in each case. The splitting of $\nu_{2}$, the degenerate methyl group vibration, is less easily extracted from the complex absorption curve in the region of $3000 \mathrm{~cm} .^{-1}$, but it does not apparently lead to a difference in the pair of more than about $80 \mathrm{~cm} .^{-1}$ As in the case of methyl alcohol, the frequencies of methyl mercaptan will be designated as follows.

Now, $\nu_{1}$ and $\nu_{2}$ (twofold degenerate, split) are valency vibrations of the methyl group. Regarding the molecule as symmetrical, with the

[^8][^9]C-S bond as the axis of symmetry, $\nu_{1}$ will involve a change in moment parallel to this axis, and $\nu_{2}$ a change in moment perpendicular to it. $\nu_{3}$ is the parallel deformation of the methyl group, and $\nu_{4}$ the twofold degenerate (split) perpendicular deformation of this group; $\nu_{5}$ is the parallel vibration arising from a vibration largely localised in the $C-S$ bond; $\nu_{8}$ the twofold degenerate (split) perpendicular deformation of this bond; $\nu_{7}, \nu_{8}$, and $\nu_{9}$, will be frequencies connected with vibrations of the S-H link; $\nu_{7}$ will be taken as the "valency" vibration of this bond; according to the value of the $\mathrm{C}-\mathrm{S}-\mathrm{H}$ angle, this vibration will be a hybrid with either the parallel or perpendicular component the more intense. If, as seems probable, the angle is close to $100^{\circ}, \nu_{7}$ will be almost completely a perpendicular type vibration; $\nu_{9}$ will be the deformation of the S-H link such that the hydrogen atom moves in

the $\mathrm{C}-\mathrm{S}-\mathrm{H}$ plane almost at right angles to the $\mathrm{S}-\mathrm{H}$ bond, i.e. roughly parallel to the $\mathrm{C}-\mathrm{S}$ axis. The remaining frequency $\nu_{8}$ will involve a vibration of the hydrogen atom perpendicular to the $\mathrm{S}-\mathrm{H}$ bond and perpendicular to the $\mathrm{C}-\mathrm{S}$ axis. This is the so-called torsional oscillation, which in the absence of a restoring force would become a free internal rotation.

Before correlating the normal modes with the infra-red absorption, it is profitable to consider the rotational properties of the molecule, The rotational structure of the $\nu_{5}$ absorption band described by Borden and Barker for methyl alcohol shows that this molecule indeed approaches very closely to a symmetric top; methyl mercaptan will be even more symmetrical. Assuming the known dimensions of the methyl group, and the covalent radii of carbon, sulphur and hydrogen given by Pauling, ${ }^{11}$ with a $\mathrm{C}-\mathrm{S}-\mathrm{H}$ angle of $100^{\circ}$, we find $I_{A} \sim 5.4 \times 10^{-40}$

[^10]and $I_{\mathrm{B}} \sim I_{\mathrm{C}} \sim 60 \times \mathrm{IO}^{-40} \mathrm{~g}$. cm. ${ }^{2}$. According to Dennison and Gerhard, ${ }^{12}$ the P and R branch spacing in a parallel band will be given by
$$
\Delta v=\frac{S}{\pi} \sqrt{\frac{k T}{I_{\mathrm{C}}}}
$$
where
$$
\log S=0.72 /(\beta+4)^{1.13} \quad \text { and } \beta=I_{\mathrm{C}} / I_{\Delta}-\mathrm{I}
$$

It follows that with methyl mercaptan the $P, R$ spacing will be close to $3 I \mathrm{~cm} .^{-1}$ This spacing will be unaffected by free rotation about the C -S bond, although the latter will probably lead to abnormal spacings in the $Q$ branches of the perpendicular type bands. With our present instrument, however, these $Q$ branches will be unresolved, and we need not further consider the perpendicular type structure.

The measurements of the Raman frequencies with liquid methyl mercaptan referred to above lead to the following intervals:

702 (strong), 803 (weak), 1055 (weak), I 319 (very weak), 1438 (weak), 2572 (strong), 2839 (medium), 2931 (strong), 2999 (medium).


Fig. 2.

According to Venkateswaran the lines 1438 and 2999 are depolarised. The lack of symmetry precludes a rigid application of selection rules in assigning

the frequencies to normal modes, but in any case little help would be obtained here since all six frequencies of a methyl halide with the symmetry $\mathrm{C}_{3 v}$ will be permitted as fundamentals in both the Raman spectrum and infra-red spectrum. From the polarisation data, however, we might expect to assign the values of 1438 and 2999 to the degenerate vibrations $\nu_{4}$ and $\nu_{2}$ respectively; and as with some other methyl compounds a Fermi degeneracy may occur between $2 \nu_{4}$ and $\nu_{1} \sim 2870$ leading to the splitting into 2839 and 2931 .

Turning now to the infra-red data, there is absorption characteristic of a parallel vibration at $I 4 \cdot 2 \mu$, i.e. $704 \mathrm{~cm}^{-1}$. The P and R branches lie at 690 and $722 \mathrm{~cm} .^{-1}$ respectively, giving a spacing of $32 \mathrm{~cm} .^{-1}$. In some of the curves there are feeble signs of the central $Q$ branch which will be present in a band of this type, but it is quite reasonable to expect such a $Q$ branch not to be revealed as a result of inadequate resolving power, especially if it is intrinsically weak. This parallel type frequency of 704 agrees closely with the Raman interval 702, and can be confidently assigned to $\nu_{5}$. Between $900-1200 \mathrm{~cm}^{-1}$ there is an intense region of absorption having the appearance of two broad and close perpendicular type bands, with centres at 957 and $1060 \mathrm{~cm} .^{-1}$ respectively. A weak Raman frequency is found at 1055, and the bands at 1060 and

957 will be assigned to $\nu_{6}^{\prime}$ and $\nu_{6}{ }^{\prime \prime}$. The band at $2597 \mathrm{~cm} .^{-1}$ is obviously to be correlated with the Raman interval 2572 and assigned to $\nu_{7}$.

Assignment of accurate values to $\nu_{1}$ and $\nu_{2}$ is less certain. The intense region of absorption around $3.4 \mu$ could not be resolved, although it coincides in position with the Raman frequency. We can perhaps safcly assume $\nu_{1} \sim 2870, \nu_{2}{ }^{\prime} \sim \nu_{2}{ }^{\prime \prime} \sim 3000$. The region $6.8 \mu$ is complex and by analogy with the frequencies of methyl chloride would be expected to embrace $\nu_{3}, \nu_{4}^{\prime}$ and $\nu_{4}{ }^{\prime \prime}$. For methyl chloride $\nu_{3}=1355$. At $7 \cdot 5 \mu$ there is a band with parallel type contour, centre at 1335 , and $P$ and $R$ branches at 1320 and 1350. Thus we may conclude $\nu_{3}=1335$, close to the Raman interval of 1319 . By comparison with methyl chloride we might expect $\nu_{4}$ to have a value close to 1460 . The most satisfactory interpretation of the contour between $1400-1500$ is to suppose that $\nu_{4}^{\prime}=1475, \nu_{4}^{\prime \prime}=1430$. Superposition of $2 \nu_{5}$ may cause interference with $\nu_{4}{ }^{\prime \prime}$. This harmonic of $\nu_{5}$ is strong in the infra-red absorption of methyl alcohol.

TABLE 1.

| Vibration. | Type. | Methyl Mercaptan Frequency. |  |  | Methyl Chloride. | Methyl Alcohol. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Raman (liq.). | Intra-red. | Adopted <br> Value. |  |  |
| $\nu_{1}$ | $\nu_{\mathrm{CH}}$ II | $\sim 2870$ | (2870) | 2870 | 2923 | 2845 |
| $\nu_{2}$ | ${ }^{2} \nu^{\text {cu }}$ | 2999 | (3000) | 3000 | 3047 | 2978 |
| $\nu_{3}$ | $\delta_{\text {CII }}$ III | 1319 | 1335 | 1335 | 1355 | 1455 |
| $\nu_{4}$ | ${ }^{2} \delta_{\mathrm{CH}} \quad 1$ | 1438 | $\left\{\begin{array}{l}1475 \\ 1430\end{array}\right.$ | $\left.\begin{array}{l}1475 \\ 1430\end{array}\right\}$ | 1460 | \{ 1477 |
| $\nu_{4}$ | $\mathrm{ClH}^{\text {ch }}$ | 143 | 1.430 | 1430 ) | 1460 | (19405) |
| $\nu_{s}$ | $\nu_{\mathrm{CS}}$ | 702 | 704 | 704 | 732 | 1034 |
| $\nu_{6}$ | ${ }^{2} \delta_{\text {cs }} \quad \perp$ | 1055 | $\left\{\begin{array}{r}1060 \\ 957\end{array}\right.$ | $\left.\begin{array}{r}1060 \\ 957\end{array}\right\}$ | 1020 | $\left\{\begin{array}{l}1340 \\ \text { ( } 230)\end{array}\right.$ |
|  |  | 2572 | $\begin{array}{r}1957 \\ \hline 297\end{array}$ | 2597 | - | (1230) 3683 |
| $\nu_{8}$ | $\delta_{\text {SH }}$ | 57 | - | ? 600 | - | ? 600 |
| $\nu_{9}$ | $\delta_{\text {SL }}$ | 805 | 803 | 803 | - | ? 1107 |

The only fundamentals not assigned are $\nu_{8}$ and $\nu_{8}$. For methyl alcohol Borden and Barker tentatively suggest $\nu_{9}=1107$. The only band with methyl mercaptan not yet identified is a feeble absorption at $12.45 \mu$. This band only appears at the highest pressures, and shows a contour with a double minimum with approximate spacing $823-790=33 \mathrm{~cm} .^{-1}$, agreeing with its being a parallel type band, and suggesting $\nu_{9}=803$. There is a Raman interval of precisely this value.

Table I summarises the above conclusions and shows their connection with other related molecules.

We should expect $v_{8}$ to have a fairly low value. As we have seen, there remains no unidentified band between $16 \mu$ and $6 \mu$. A very weak absorption was noticed in the region of $8 \mu$ in some of the measurements, but this does not appear to be real. If $\nu_{8}$ is perceptibly absorbed in the infra-red therefore, it would have to lie to the long wave-length side of $16 \mu$. This would be in agreement with the result of Borden and Barker for methyl alcohol, where a peculiar absorption between $16-24 \mu$ was attributed to $\nu_{8}$. Present circumstances have made it impossible so far to examine this region, but it is hoped to do so in the near future.

In Table II interpretations are suggested for the combinations and overtones observed in the infra-red. Each explanation seems satisfactory. Some information about the torsional vibration, if it exists, might be obtained from specific heat measurements, but these are not available.

TABLE II.

| Wave-length ( $\mu$ ). |  | Wave Number (cm. ${ }^{-1}$ ). | Interpretation. | Calculated Frequency. |
| :---: | :---: | :---: | :---: | :---: |
| 6.58 | w.* | 1520 | $\nu_{56}+\nu_{9}$ | 1507 |
| 6.06 | v. w. | 1650 | $\nu_{5}+\nu_{6}^{\prime \prime}$ | 1661 |
| $5 \cdot 69$ | w. | 1760 | $\nu_{5}+\nu_{8}{ }^{\prime}$ | 1764 |
| $4 \cdot 92$ | w. | 2035 | $\nu_{6}+\nu_{3}$ | 2039 |
| $4 \cdot 7$ | v. w. | 2128 | $2 v_{0}$ | 2120 |
| $4 \cdot 4$ | v. w. | 2273 | $\nu_{3}+\nu_{8}{ }^{\prime \prime}$ | 2292 |
| $4 \cdot 21$ | v. w. | 2375 | $\nu_{3}+\nu_{8}^{\prime}$ | 2395 |
| $3 \cdot 41$ | v. s. | 2933 | Various $\nu_{\text {Ch }}$ combinations |  |
| $2 \cdot 72$ | m. | 3676 | $\nu_{2}+\nu_{5}$ | 3685 |
| $2 \cdot 52$ | w. | 3968 | $\nu_{2}+\nu_{8}{ }^{\prime \prime}$ | 3957 |
| 2.45 | w. | 4082 | $\nu_{2}+\nu_{0^{\prime}}^{\prime \prime}$ | 4060 |
| $2 \cdot 265$ | s. | 4376 | ? $\nu_{2}+\nu_{4}^{\prime \prime}$, | 4430 |
| $2 \cdot 285$ | s. | $44^{15}$ | ? $\nu_{2}+\nu_{4}^{\prime}$ | 4475 |
| $\underline{1.94}$ | w. | 5155 | $2 v_{7}$ | 5194 |

* w. weak, v. w. very weak, m. medium, s. strong, v. s. very strong.

It is hoped, if conditions permit, shortly to examine the structure of some of the bands, using a grating spectrometer. This may give further information about the molecular structure.

## Summary.

The infra-red absorption spectrum of methyl mercaptan vapour has been studied between $\mathrm{I}-\mathrm{I} 6 \mu$. The wave-lengths of the bands observed have been correlated with the known Raman frequencies. A satisfactory assignment of the different magnitudes to the normal modes has been achieved, with one exception. The missing frequency is that corresponding to the internal torsional motion about the carbon-sulphur bond. The band contours are compatible with the molecular structure assumed. The normal frequencies have been compared with those of related molecules.

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# A RELATION BETWEEN THE ACTIVATION ENERGIES OF REACTIONS IN SOLUTION AND THE DIELECTRIC CONSTANTS OF THE MEDIA. THE MEASUREMENT OF ACTIVATION ENERGIES IN SOLUTION. 

By David P. Evans and H. O. Jenkins.

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The influence of the medium upon reaction velocity in solution has been studied for many years. The work of Menschutkin ${ }^{1}$ on the reaction between amines and alkyl halides in different solvents has been followed by similar studies by several workers, and although numerous attempts have been made to establish relationships between reaction velocity and some physical property of the solvent, as pointed out by Moelwyn-Hughes, ${ }^{2}$ these have met with little success. This is not surprising in view of the fact that the velocity coefficient is affected by at least two variables now recognised as (I) the probability factor $P$, and (2) the activation energy $E$, of the kinetic equation

$$
k=P Z \cdot \mathrm{e}^{-E / \boldsymbol{n} T} .
$$

As a result, in most of the more recent work, the effect of the solvent upon $E$ and $P Z$ has been studied separately. ${ }^{3}$ Moelwyn-Hughes ${ }^{4}$ has put forward a method of determining the influence of ionic strength of the medium upon the activation energy and the probability factor of several types of reactions.

The acid and alkaline hydrolyses of substituted benzoic esters have been studied in different solvents by several investigators, ${ }^{5}, 6,7,8,9$ and the results of these researches lead to some interesting conclusions. The present paper is concerned with some theoretical considerations bearing on these reactions, together with some observations regarding reactions in general.
H. O. Jenkins ${ }^{10}$ has recently shown that for the alkaline hydrolysis of benzoic esters a linear relation holds between the activation energy and the electrostatic potential $\psi=\mu \cos \theta / r^{2}$ at the carbon to which the carbethoxyl group is attached. The plot of $E$ against $\psi$ has a slope approximating to the value $N e$ (I Faraday), which confirms ${ }^{11}$ the electrostatic interpretation of the variation in activation energy for this reaction, as put forward by Hinshelwood, Laidler and Timm. ${ }^{12}$ These latter

[^11]authors ${ }^{13}$ suggested that the activation energy is made up of two factors, the bond energy and the repulsion energy of which the main portions are non-classical, but that variations of both due to substituents may be expressed in classical electrostatic terms. For the alkaline hydrolysis of benzoic esters, therefore, the change in activation energy due to substituents is accounted for in terms of the extra work needed to bring up the hydroxyl ion against the dipole field of the substituent. Further, since Timm and Hinshelwood ${ }^{8}$ found that the relation $\Delta E_{\text {acld }}=\alpha \Delta E_{\text {alkaline }}$ holds for the acid and alkaline hydrolyses of these esters in a given solvent, it follows that the variations in $E$ for the acid hydrolysis can also be interpreted in terms of the change in the electrostatic repulsion between the ester and the water molecule.

When we go from one solvent to another, the complete expression for the electrostatic potential $\psi=\mu \cos \theta / \epsilon r^{2}$ must be employed, which includes $\epsilon$, the dielectric constant of the solvent. It follows that a

## TABLE $I$.

## Activation Energies in Acetone-Water.

| C.c. $\mathrm{H}_{2} \mathrm{O}$ per 100 c.c. soln. | 55 | 50 | 45 | 40 | 35 | 30 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Wt. \% acctone | 41 | 45 | 50 | 56 | 64 | 75 |
| $\epsilon_{20}{ }^{\circ}$ | $55 \cdot 3$ | $52 \cdot 7$ | 49.5 | $45 \cdot 7$ | $40 \cdot 5$ | 33.5 |
| $x / \epsilon_{20}{ }^{\circ}$ - | 0.018 | 0.019 | 0.02 | $0 \cdot 022$ | 0.025 | -0,03 |
| $E$ (benzoate) (cals.) | 13,820 | 13,970 | 14,070 | 14.330 | 14,880 | 15,840 |
| $E$ (m-nitrobenzoate) | - | - | 13.140 | 13,260 | 13.330 | 13,370 |

Activation Energles in Alcohol-Water.

| C.c. $\mathrm{H}_{2} \mathrm{O}$ per 100 c.c. soln. | 60 | 55 | 50 | 40 | 30 | 20 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Wt. \% alcohol . | 35 | 40 | 42 | 54 | 65 | 76 |
| $\epsilon_{200}$ | $59 \cdot 5$ | $56 \cdot 2$ | 55 | 48 | $4 \mathrm{r} \cdot 8$ | $35 \cdot 7$ |
| 1/ $\epsilon_{20}$ | 0.017 | 0.018 | 0.018 | 0.021 | 0.024 | 0.028 |
| $E$ (benzoate) (cals.) | 14.760 | 15.330 | 15,750 | 16,460 | 17,040 | 17.400 |
| $E$ (m-nitrobenzoate) |  |  |  | 14,290 | 15,210 | 15,900 |

linear relation would be expected to hold between the activation energy and the reciprocal of the dielectric constant for the hydrolysis of any one benzoic ester in various (aqueous) solvents. Fortunately data are available to test this prediction. Harman ${ }^{9}$ has measured the activation energies for the alkaline hydrolyses of benzoic and of $m$-nitrobenzoic esters in various acetone-water and alcohol-water mixtures, and Akerlöf 14 has measured the dielectric constants of such mixtures. The results are shown in Table I, and are illustrated in the figure.

The plot of $E$ against $I / \epsilon_{20^{\circ}}$ is approximately linear for both esters in the acetone-water and in the alcohol-water mixtures, but the plot for any one ester is not continuous for alcohol and acetone-water solvents. This indicates that the effect of the solvent added to the water is specific. We therefore tentatively suggest that the equation

$$
E=E_{\mathrm{B}}+E_{\mathrm{X}} / \epsilon_{20^{\circ}}
$$

will represent with reasonable accuracy the variation of the activation energy for the alkaline hydrolysis of any $m$ - or $p$-substituted benzoic ester in passing from solvent to solvent of similar type. Here we regard alcohol-water as being of a different type compared with acetone-water; by using different mixtures of the same pair of liquids changes in factors other than the dielectric constant are avoided as far as possible.

Of the two factors which contribute to the activation energy, it appears reasonable to assume that the bond-stretching energy, although altered by the presence of a substituent (compare Hinshelwood, Laidler and Timm ${ }^{12}$ ) is, within certain limits, independent of the solvent environment (compare Moelwyn-Hughes ${ }^{4}$ ). On the other hand, the magnitude of the repulsion energy would be expected to be governed by the dielectric constant of the medium. Now, the above equation divides the activation energy into two parts in this fashion, and extrapolation to $I / \epsilon=0$ yields values for the term $E_{\mathrm{B}}$ which may be taken to represent the magnitude of the bond-stretching energies for each ester in (a) alcohol-water, and (b) acetone-water solvents. The difference between the values of the activation energies and the bond-stretching energies (i.e. $E-E_{\mathrm{B}}$ ) gives the magnitude of the repulsion energies $E_{\mathrm{R}}\left(=E_{\mathbf{X}} / \epsilon\right)$ in each solvent. Values of $E_{B}, E_{R}$ and $E$ are given in Table II.

TABLE II.

| Ester. | $E_{B}$ (cal.). | $E$ (cal.). | $E_{\mathrm{R}}$ (cal.). |
| :---: | :---: | :---: | :---: |
|  |  | ( $\epsilon=33.5$ ) | ( $\epsilon=33.5$ ) |
| Ethyl benzoate . | 11,000 | I5,840 | 4,840 ${ }^{\text {acetone }}$ |
| Ethyl m-nitrobenzoate | 12,500 | $\begin{array}{r} I 3.370 \\ (\epsilon=42) \end{array}$ | $\begin{aligned} & 870\} \text { water } \\ & (6=42) \end{aligned}$ |
| Ethyl benzoate . | 9,000 | 17,040 | 8,000 ${ }^{\text {alcohol }}$ |
| Ethyl m-nitrobenzoate | 10,000 | I5,210 | 5,000 $\}$ water |

The extent to which $E$ varies with solvent influence depends upon the ratio $E_{\mathrm{R}} / E$. In all the above cases the repulsion energies $E_{\mathrm{R}}$ are sufficiently large to show some solvent dependence. It is noteworthy, however, that in the one instance where $E_{R}$ is a comparatively small fraction of the total activation energy, viz., for the $m$-nitrobenzoate in acetone-water, the variation of $E$ with $I / \epsilon$ is also very small.

There are many known reactions where the repulsion energy is too small a fraction of the total activation energy to allow of variation of $E$ with solvent conditions. Such examples may be found in reactions between neutral molecules, which have the same activation energy in several solvents, e.g. the decomposition of nitrogen pentoxide in chloroform, carbon tetrachloride, and certain other solvents, ${ }^{15,16}$ the change of $d$-pinene into dipentene, ${ }^{17}$ the decomposition of chlorine monoxide, ${ }^{18}$ and the bimolecular addition of acraldehyde to cyclopentadiene. ${ }^{19}$ The fact that in several of these reactions the activation energy is the same in the gas phase as in solution is good support of the suggestion that the energy is concerned only with bond stretching and has no component which is influenced by solvent conditions. The solvent will have an

[^12]effect upon the energy of activation of a reaction only when the latter has a repulsion term of sufficient magnitude, and this condition will be obeyed in the following types of reactions $(a)$ ionic reactions, $(b)$ reactions between a neutral molecule and an ion, and (c) reactions between neutral molecules, one of which gives up an ion to the other on collision, e.g. the attack of a water molecule on an ester during acid hydrolysis, ${ }^{11}$ or reaction between a weak base and an alkyl halide. Briefly, we follow the schematisation given by Hinshelwood, Laidler and Timm. ${ }^{12}$

It has been stated by Timm and Hinshelwood ${ }^{8}$ that " in the acid hydrolysis the activation energy of a given (benzoic) ester increases as we go from alcohol-water to acetone-water solvent, whereas in alkaline hydrolysis this trend is reversed." This observation was based on a comparison of the activation energies for the acid hydrolysis in $56 \%$ acetone and $56 \%$ alcohol, with those for the alkaline hydrolysis of the same ester in $56 \%$ acetone ${ }^{6}$ and in $85 \%$ alcohol. ${ }^{5,7}$. It is interesting to note that if consideration is given to the change in the dielectric constants of the media then the apparent difference in the trend of $E$ on changing from solvent to solvent disappears. This is made clear by reference to Table III.

TABLE III.

| Authors. | Wt. \% Acetone or Alcohol. | Ester. | E Cals. |
| :---: | :---: | :---: | :---: |
| Newling and | $56 \%$ acetone | benzoic | 13,750 [45'7 |
| Hinshelwood ${ }^{\text {c }}$ | $56 \%$ acetone | $p$-nitrobenzoic | 12,500 145.7 |
| Ingold and | $85 \%$ alcohol | benzoic | 17,700 \{ 31.4 |
| Nathan ${ }^{5}$ | $85 \%$ alcohol | $p$-nitrobenzoic | $14,500\left\{\begin{array}{l}31 \cdot 4 \\ 314\end{array}\right.$ |
| Timm and | $56 \%$ acetone | benzoic | 20,250 \{ $45 \cdot 7$ |
| Hinshelwood ${ }^{8}$ | $56 \%$ acetone | $p$-nitrobenzoic | 19,650 $4.45 \cdot 7$ |
| Timm and | $56 \%$ alcohol | benzoic | 19,630 ¢ 53.7 |
| Hinshelwood ${ }^{\text {8 }}$ | $56 \%$ alcohol | p-nitrobenzoic | 17.520 (53.7) |

Since the dielectric constant of $85 \%$ alcohol is appreciably smaller than that for $56 \%$ acctone, the decrease in $E$ for a given ester in passing from the former to the latter solvent (alkaline hydrolysis) is in the direction expected from the equation $E=E_{\mathrm{B}}+E_{\mathrm{X}} / \epsilon$. On the other hand, since acid and alkaline hydrolyses are both class $B$ reactions according to the classification of Ingold and Rothstein, ${ }^{20}$ we should expect the change of activation energy for acid hydrolysis to follow the same direction on changing the dielectric constant as that followed by alkaline hydrolysis. It would appear, therefore, that in passing from $56 \%$ acetone to $56 \%$ alcohol the activation energies for the acid hydrolysis of benzoic and of $p$-nitrobenzoic esters decrease mainly as a result of the increased dielectric constant. We venture to suggest that if the dielectric constant were to change in the same direction as occurs in going from $56 \%$ acetone to $85 \%$ alcohol, then the activation energies for the acid hydrolyses would increase.

We realise that the lines shown in the graph are of necessity approximate, and further accurate work must be forthcoming before any precise

[^13]claims may be made. However, we consider it worthy of note that the values of $E_{\mathrm{B}}$ and of $E_{\mathrm{R}}$ for the $m$-nitrobenzoic ester in both solvents when compared with the corresponding values for ethyl benzoate are in the direction anticipated from the ideas put forward by Hinshelwood, Laidler and Timm. ${ }^{12}$ Moreover, if the figure $10,000 \mathrm{cal}$. is taken as the order of magnitude of the bond-stretching energy it is possible to calculate the magnitude of the bond stretching by application of the equation ${ }^{21}$
$$
2 V=k(\Delta r)^{2}
$$
in which $k$ is the bond force constant, $\Delta r$ is a small displacement from the equilibrium position, and $V$ represents the encrgy given to the bond. The equation is applicable to small displacements from the equilibrium positions in diatomic molecules, but is probably sufficiently accurate to give us the order of magnitude of the bond stretching in the cases considered. Assuming the value 0.5 megadynes per cm. for $k$ (see Sidgwick ${ }^{22}$ ) we find that for an energy contribution of $10,000 \mathrm{cal}$. the bond stretching $\Delta r$ is 0.2 A . This value is small, but the amount of stretching required to break a covalent link is low. It is interesting to observe that the above value of the bond extension necessary to form the activated complex, is of the same order as the difference between the single and double, and between the double and triple carbon-oxygen bonds. The actual distances apart of these atoms in the "pure" bonds are as shown below. ${ }^{23,} 24,25$

| $C-O$ | $C=O$ | $C=O$ |
| :---: | :---: | :---: |
| 1.43 | 1.24 | I•II A. |

Wynne-Jones ${ }^{26}$ has given evidence of a relation between $\log K$ and $I / \epsilon$ for equilibrium constants (i.e. the strengths) of acids in certain solvents, and several other workers have established a connection between velocities of reactions and equilibrium constants in a given solvent. ${ }^{27}, 28,29$ Dippy and Watson ${ }^{30}$ showed that "a connection of roughly linear character exists, in a number of cases, between the values of $\log k$ (velocity coefficient) for the same reaction of a series of $m$ - and $p$-substituted benzene derivatives and those of $\log K$ for the corresponding benzoic acids " in water. It follows, therefore, if $\log K$ varies directly with the reciprocal of the dielectric constant that $\log k$ might vary similarly. Now, the usual method for determining activation energies of reactions in solution involves a temperature range of $30^{\circ}$ to $50^{\circ}$, and in view of the variation of dielectric constant with temperature, it appears that for reactions of the type mentioned on page 82 I , where solvent effect upon $E$ may be appreciable, the experimental values of the activation energy are not a true measure of the energy required to form the transition complex. Thus the dielectric constant of $50 \%$ acetone-water mixture decreases by 6.7 for a $30^{\circ}$ rise in temperature ${ }^{14}$ from $20^{\circ}$, whilst reference to Table I for ethyl benzoate indicates that

[^14]the activation energy alters by approximately 900 cal . when the dielectric constant is changed from $33 \cdot 5$ to $40 \cdot 5$. To what extent does this possible variation of $E$ with $\mathrm{I} / \epsilon$ affect the experimental evaluation of the activation energy for reactions which are markedly affected by solvent change of the type herein studicd? The problern is somewhat similar to that encountered in the temperature solution method for measuring dipole moments, which has now been abandoned ${ }^{31}$ because the polarisation was dependent on the dielectric constant. In both the evaluation of dipole moments and energies of activation in solution, the plot of the experimental values of the polarisation in the former, and of the logarithm of the velocity constant in the latter against the reciprocal of the absolute temperature give good straight lines. The intercepts, however, must be incorrect. This means that owing to the variation of $E$ with $I / \epsilon$ (and hence with $\mathrm{I} / T$ ) the plots of $\log k$ against $\mathrm{I} / T$ for certain reactions yield lines of low slope and low intercept, i.e. yield low values of both the activation energy and $\log P Z$. The actual deviation from the true "gas" value for the activation energy is probably not very large, but it may be appreciable in some reactions. In reactions of types (a), (b) and (c), page 82I, we should expect deviations from the Arrhenius line when the temperature range is large, and it is significant that the list of reactions given by LaMer and Miller, ${ }^{3}$ which show deviation are of these types. It is surprising that so few reactions show appreciable deviation from linearity when $\log k$ is plotted against $1 / T$, and it would appear that opposing influcnces are at work which generally result in a good straight line.

The above considerations suggest that the recent practice of comparing the energies of activation for the same reaction for a series of similarly constituted compounds is theoretically disputable. Nevertheless, since in all these investigations the same solvent is used for the series of compounds chosen, each activation energy will be subject to approximately the same (large or small) error, and therefore qualitative comparison of effects of substituents upon $E$ is justified.

## Summary.

A relation of the form $E=E_{\mathrm{B}}+E_{\mathbf{X}} / \epsilon$ has been suggested between activation energies in solution and the dielectric constants of the media. The equation permits of the evaluation of the order of magnitudes of the bond-stretching and repulsion energies. Further, the variation of activation energy with the reciprocal of the dielectric constant is shown to be expected only when the repulsion energy, $E_{R}$, is a sufficiently large fraction of the total activation energy. The validity of the usual method of determining activation energies for reactions in solution is questioned.

Technical College, Cardiff.
${ }^{31}$ See Jenkins, Trans. Faraday Soc., 1934, 30, 739.

## WOOD-WATER RELATIONSHIPS. V. THE HYDROSTATIC COMPRESSIBILITY OF THE WOODWATER AGGREGATE.

By Wilfred W. Barkas.

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Wood is a cellular material of complex structure, so that while it is permissible for practical purposes to treat it as a continuous medium and on that assumption to calculate its elastic constants from mechanical tests, it is evident that the constants of the solid material of which the wood is composed may be very different from those of the gross wood. This solid material is an anisotropic hygroscopic gel which we shall term the " wood-water aggregate" in order to stress the importance of the water constituent and at the same time to be suitably non-committal as to the separate contributions of the dry wood substance and the water in determining the properties of the material as a whole. For brevity we refer to this as the " aggregate."

We shall show how the hydrostatic compressibility $\beta$ of the aggregate may be calculated, but, owing to the limited accuracy of the available data, $\beta$ will, in fact, be deduced from the slopes of the $(p ; V)$ curves. A knowledge of $\beta$ is of importance to the general study of the mechanical properties of wood, but particularly to cases where, e.g., the wood has been compressed, disintegrated or impregnated, so that the elastic constants obtained on the natural material are no longer applicable.

The only calculation of $\beta$ of the aggregate appears to be that of Volbehr ${ }^{1}$ at $20^{\circ} \mathrm{C}$. on spruce wood flour, extracted with alcohol and water, and was made from his observations on the specific volume, :specific heat and heat of wetting. His calculation applies only to the :saturated fibres and yields a value of $21.9 \times 10^{-6}$ per bar. He takes the saturated moisture content to be 0.3715 g . water per g. dry wood. This single determination gives no indication of the change of $\beta$ with moisture content which is essential if practical use is to be made of the results. Volbehr's value will be used as a check on the results obtained below.

## Theory.

The hydrostatic compressibility is given by

$$
\begin{equation*}
\beta=-\frac{\mathrm{I}}{V}\left(\frac{\partial V}{\partial p}\right)_{m} \tag{I}
\end{equation*}
$$

where $V$ is the volume of the aggregate and $p$ the pressure applied. In this paper $V$ will refer to the volume of aggregate containing I $g$. of dry material and $m$ g. of water, and $p$ is in bars ( I bar $=10^{6}$ dynes/sq. cm . or very nearly i atmosphere). We shall also be discussing solutions of

[^15]which the density $p$ or specific volume $\sigma$ and concentration $x$ (g. solute/ g. solution) are usually given in tables. Thus we require the relations
\[

$$
\begin{gather*}
m=\frac{\mathrm{I}-x}{x} \\
V=\frac{\sigma}{x}=\sigma(\mathrm{I}+m) \tag{2}
\end{gather*}
$$
\]

Porter's equation ${ }^{2}$ for the osmotic pressure of solutions,

$$
\int_{h_{1}}^{p_{m}} \begin{align*}
& h_{m} p_{m}
\end{aligned}-\int \begin{aligned}
& p_{0}  \tag{3}\\
& u d p_{0} \\
& h_{0}
\end{aligned}=\int_{h_{1}}^{h_{0}} \begin{aligned}
& 0 \mathrm{~d} h \\
& h_{1}
\end{align*}
$$

gives the relation between the hydrostatic pressures $p_{m}$ and $p_{0}$ to be applied to a solution (of constant moisture content $m$ ) and to free water respectively in order that their vapour pressures, initially $h_{1}$ and $h_{0}$, may be made equal. At a common vapour pressure $h$ this equation gives,

$$
\begin{equation*}
s \mathrm{~d} p_{m}=u \mathrm{~d} p_{0}=v \mathrm{~d} h \tag{4}
\end{equation*}
$$

In the above, $s=\left(\frac{\partial V}{\partial m}\right)_{p}=$ change in volume of the solution per unit change in moisture content under constant pressure $p, u=$ specific volume of liquid water under constant pressure $p_{0}$ and $v=$ specific volume of water vapour under vapour pressure $h$.

Equation (3) which is exact for any solution of which only one constituent is volatile, may be equally applied to gels fulfilling this condition, e.g., to the wood water aggregate. For the range of pressures considered here, zero may be substituted for $h_{1}$ and $h_{0}$ in the first two integrals of (3) and for normal temperatures, $v$ may be written as $R T / M$ h. If as an approximation it is assumed that $\beta=0$ and $s=u$, then $u \mathrm{~d} p_{m}=v \mathrm{~d} h$ or

$$
\begin{equation*}
p_{m}=-\frac{R T}{M \bar{u}} \log h_{1} / h_{2} \tag{5}
\end{equation*}
$$

Where $h_{1}$ and $h_{2}$ are the initial and final vapour pressures, and $\bar{u}$ is the mean specific volume of the water. This is Katz's well-known equation for the swelling pressure of gels. Since it is the compressibility, we propose to calculate, it will obviously be inadmissible to put $\beta=0$, but we shall have occasion to refer to (5) later.

In the absence of reliable data on the compressibility of gels, the method to be used in determining $\beta$ will be developed from a consideration of solutions.

Solutions.-Figs. I and 2 show as full lines the $(p ; V)$ curves ${ }^{3}$ for NaCl and $\mathrm{H}_{2} \mathrm{SO}_{4}$ solutions at $25^{\circ} \mathrm{C}$. for various concentrations and, as broken lines, values of $h / h_{0}$ calculated by means of Porter's equation. In Fig. I calculations of $h / h_{0}$ have been possible up to very high values

[^16]

Fig. 1.


Fig. 2.
since Adams gives changes of $\beta$ up to 10,000 bars, but the range of $m$ is limited owing to poor solubility. In Fig. 2, on the other hand, a full range of $m$ is available, since $\mathrm{H}_{2} \mathrm{SO}_{4}$ is soluble in all proportions, but $\beta$ is given by Gibson only at 1000 bars, thus limiting the range of pressures over which $h / h_{0}$ can be calculated with :accuracy.

A small portion of either of these figures is enlarged in Fig. 3. Consider three ways of raising the vapour pressure of the solution at A from $h$ to $h+\Delta h$ : (I) At constant pressure, add $\Delta m \mathrm{~g}$. water, increasing the volume by $\Delta V_{D}$ to the point B. (2) At constant moisture content, increase the pressure by $\Delta p_{m}$ and decrease the volume by $\Delta V_{m}$ to D. (3) At constant volume


Fig. 3. add a small amount of water and increase the external pressure by $\Delta p_{V}$ to the point $C$. Then by similar triangles

$$
\begin{equation*}
\frac{E C+A C}{A C}=\frac{D E+B A}{B A} \text { or } \frac{\Delta p_{m}}{\Delta p_{v}}=\mathrm{I}+\frac{\Delta V_{m}}{\Delta V_{g}} \tag{6}
\end{equation*}
$$

but $\Delta V_{m}=-V \beta \Delta p_{m} ; \quad \Delta p_{m}=\frac{v \Delta h}{s} ;$ and $\Delta V_{\mathcal{D}}=s \Delta m$, hence by suitable substitutions, $v\left(\frac{\partial h}{\partial p}\right)_{V}=\left(\frac{\partial V}{\partial m}\right)_{h}$ or $=s-V \beta \frac{v}{s}\left(\frac{\partial h}{\partial m}\right)$, where $\left(\frac{\partial V}{\partial m}\right)_{h}$ is the change in volume on removing $\mathrm{d} m \mathrm{~g}$. of water at constant vapour pressure.

Returning to Figs. I and 2, it will be seen that the vertical distance $\Delta p_{V}$ between any two $h / h_{0}$ lines appears to be constant at all concentrations of the solution. This has been confirmed on these and other solutions by drawing these curves on an enlarged scale. At infinite dilution we arrive at pure water, in which case the $h / h_{0}$ lines are horizontal and $\Delta p_{m}=\Delta p_{v}$. But for water we must substitute $p_{0}$ for $p_{m}$, hence $\Delta p_{v}=\Delta p_{0}$ and (6) becomes
or

$$
\begin{array}{r}
u=\left(\frac{\partial V}{\partial m}\right)_{h} \\
u=s-\frac{R T}{M} \frac{V \beta}{s h}\left(\frac{\partial h}{\partial m}\right)_{p} \tag{8}
\end{array}
$$

The quantities in (8) are readily obtainable for unstressed solutions, i.e. at vapour pressures less than saturation, so that values of $u$ in tension may be calculated which should give a reasonable extrapolation from the known values of $u$ in compression if the observation is correct. This $u$ is the specific volume of any water which may be held at reduced vapour pressure in the fine capillaries of porous gels, the capillary wall acting as its own semi-permeable membrane.

In order to obtain $u$ under tension for the full range of vapour pressures at $20^{\circ} \mathrm{C}$. (the temperature of Volbehr's experiments) the above $\mathrm{H}_{2} \mathrm{SO}_{4}$ data are used. Small temperature and pressure corrections for $\beta$ are necessary as ( 8 ) implies that this be measured at zero pressure,
-and for these it will be sufficiently accurate to assume that $\beta$ of the solution changes between 1000 bars at $25^{\circ} \mathrm{C}$. and zero pressure at $20^{\circ} \mathrm{C}$. in the same ratio as does water between these temperatures and between 1000 bars and 12.5 bars, the lowest pressure given by Amagat. ${ }^{3 d}$ This ratio is $49 \cdot \mathrm{I} / 39 \cdot 7=\mathrm{I} \cdot 236$, and affects $(u-s)$ in this proportion; the effect on $u$ itself is therefore much smaller. A more serious uncertainty appears at humidities below 25 per cent., where differences occur between the vapour pressures published by Landolt Bornstein ${ }^{3 \text { e }}$ (Regnault's values) and in the International Critical Tables. ${ }^{3 f}$ The effect of these discrepancies on $u$ in tension is shown in Fig. 4. In addition, this figure gives $u$ in compression from Bridgman, ${ }^{3}$ c while the straight line shows the slope of $\beta$ for water at $12 \cdot 5$ bars. It will be seen that Regnault's vapour pressures give an


Fig. 4. almost rectilinear ( $p_{0} ; u$ ) relation in tension which is also a perfect fit with $\beta$ at 12.5 bars, while the I.C.T. vapour pressures are equally possible in giving a constantly decreasing $\beta$ with decreasing tension, extrapolating smoothly to the continued decrease of $\beta$ with increasing compression. There seems no way of choosing between the two but, as they coincide up to tensions of 1000 bars, both support the original observations that $(\partial h / \partial p)_{V}$ is constant at constant $h$, and that this may be applied also to water.

If equation (8) is true, it should yield the same( $p_{0} ; u$ ) curve from any solution whose compressibility is known. Similar curves were therefore calculated from data on NaCl , KCl and $\mathrm{CaCl}_{2}$ solutions. At small tensions (to say 400 bars) these give $u$ in good agreement with Fig. 4, but thereafter the values depend on the solution used, and tend to become rather smaller than those shown for $\mathrm{H}_{2} \mathrm{SO}_{4}$ at concentrations near the limit of solubility. Though the agreement is satisfactory if considered as a method of determining $u$, it should be closer if the accuracy to which $\beta$ is given in the literature is a true reflection of the accuracy attained in its determination. That this may not be the case is suggested by the decision of the I.C.T. to give no values of $\beta$ for solutions, on the ground that it is impossible to reconcile conflicting values. Alternatively the discrepancies may be due to a lack of constancy of $(\partial h / \partial p)_{V}$ at concentrations near the limit of solubility. For $\mathrm{H}_{2} \mathrm{SO}_{4}$ solutions there is no limit of solubility, and Regnault's vapour pressures, which give the simplest extrapolation from the compression values of $u_{\text {. }}$. will be used in what follows.

Before discussing the use to which these values of $u$ may be put, two other points of interest emerge. Firstly, if, as we now presume, $\mathrm{d} p_{V}=\mathrm{d} p_{0}$ then $p_{V}$ is also given by Katz's equation (5) above. It was there shown that the Katz equation could be obtained from Porter's on the assumption that the solution was incompressible. We now see that it can also be obtained, even allowing for the compressibility, provided the inevitable reduction in volume is counteracted by the addition of a small amount of water. Secondly, equation (7), which is an alternative and precise expression of the observation that $(\partial h / \partial p)_{V}$ is constant at constant $h$, may be integrated to

$$
\begin{equation*}
\left(V_{1}-V_{2}\right) h=u\left(m_{1}-m_{2}\right) \tag{9}
\end{equation*}
$$

since $u$ is also constant at constant $h$. This shows that if the concentration of a solution is changed, while the pressure on it is continually adjusted so as to keep the vapour pressure constant, then the change in volume of the solution is equal to the volume of water removed or added. This condition would be achieved in practice by slowly increasing the load on a solution in a constant humidity, and is approximately what must occur in syneresis where the gel and liquid, being in contact, must exert the same vapour pressure. It is not without significance to the present discussion that the reduction in volume of the gel in syneresis has been found in fact to be equal to the volume of liquid expelled. ${ }^{4}, 5$ The more common case, in which the solution is subjected to a constant pressure (or to zero pressure in the case of natural evaporation), the removal of water results in a volume change in the solution of $\int_{m_{2}}^{m_{2}} \mathrm{~d} m$ whereas the volume of water removed is $\int_{m_{1}}^{u} \mathrm{~d} m$, the former being always the smaller. $m_{1}$

## Gels.

It is now proposed to assume that equation (7) may be applied also to gels, and to see how far the assumption is justified by the results obtained.

Equation (8) may be rewritten as

$$
\begin{equation*}
-\beta=\frac{M}{R T} \frac{h(u-s)}{V}\left(\frac{\partial V}{\partial h}\right)_{p} \tag{i0}
\end{equation*}
$$

and used to calculate the compressibility of any gel for which the specific volume and vapour pressure are known at each moisture content. Such data usually apply to the unstressed gel, so that (io) will only give us $\beta$ at zero stress, but equation (9) gives a method of extending the calculation to finite pressures also.

If, as in Fig. 5, $V_{0}$ be the original volume of the gel, at moisture content $m$, which must be subjected to pressure


Fig. 5. $p_{m}$ in order to raise its vapour pressure to $h$, and if subscript $n$ is used to denote properties of an unstressed gel in equilibrium with the same vapour pressure $h$ also, we have by (9), the

[^17]total strain is $\left(V_{0}-V\right)$, where
\[

$$
\begin{equation*}
V=V_{n}-u\left(m_{n}-m\right) \tag{II}
\end{equation*}
$$

\]

or by differentiating and substituting $s_{n}$ for $\mathrm{d} V_{n} / \mathrm{d} m_{n}$

$$
\begin{equation*}
-\left(\frac{\partial V}{\partial h}\right)_{m}=\left(u-s_{n}\right) \frac{\mathrm{d} m_{n}}{\mathrm{~d} h}+\left(m_{n}-m\right) \frac{\mathrm{d} u}{\mathrm{~d} / h} \tag{I2}
\end{equation*}
$$

giving the change of volume with vapour pressure at constant moisture content. From (6)

$$
\begin{equation*}
u-s=-\left(\frac{\partial V}{\partial h}\right)_{m}\left(\frac{\partial h}{\partial m}\right)_{v} \tag{I3}
\end{equation*}
$$

so that, knowing $u$, we may obtain $s$ by substituting for $(\partial V / \partial h)_{m}$ from (12). Finally, equations (4), (I2) and (I3) serve to calculate $\beta$.

This procedure demands greater accuracy than is available in data on wood. We may, however, proceed graphically. From equation (5) we know the pressure $p_{v}$ required to raise a gel at constant volume $V_{0}$ to any vapour pressure, so that the complete ( $p ; h$ ) system of curves can be constructed independently of any calculations of strain. On these the strained volumes $V$ obtained by (II) are plotted on their appropriate $h$ line and the external pressure $p_{m}$ is then read from the graph. Finally, $\beta$ is obtained from the slope of the resultant $(p ; V)$ curve.

## Wood-Water Aggregate.

Volbehr's calculation of $\beta$ of the saturated fibres ${ }^{1}$ involved no measurement of vapour pressure, whereas this forms the basis of the present method. His values of $\sigma$, which were measured on samples reaching equilibrium by adsorption, may therefore be used in conjunction with a suitable adsorption


Fi6. 6. vapour pressure isothermal to test the agreement between the methods,* though at high moisture contents his values of $\sigma$ become very uncertain as he himself admits. The isothermal used here is that given by Filby and Maass ${ }^{6}$ for extracted spruce at $20^{\circ} \mathrm{C}$. Taking Volbehr's value of

$$
m=0.3715
$$

as the saturation moisture content on adsorption (a value compatible with the isothermal used), Fig. 6 gives the ( $p ; V$ ) curve at this moisture content calculated by the method just described. The sudden curvature near zero tension may be put down to the uncertainty of $\sigma$ at high moisture contents, $\dagger$ so that the general slope of the curve may be taken giving

[^18]$\beta=26 \times 10^{-6}$ per bar. Considering that $\beta$ is likely to decrease with decreasing tension, (see footnote $\dagger$ above), this value is in very good agreement with Volbehr's figure of $21.9 \times 10^{-6}$ per bar.

This agreement is strong evidence that the original assumption leading to (7) is correct in the case of gels also, and that we shall be justified in constructing curves at other moisture contents. To do this we use the more reliable values of $\sigma$ given by Stamm and Seborg ${ }^{7}$ at $30^{\circ} \mathrm{C}$. Here, too, uncertainties exist, as the nearest isothermal available is one obtained on unextracted spruce at $23^{\circ} \mathrm{C}$. in this Laboratory; $u$ is calculated at $25^{\circ} \mathrm{C}$., the temperature of the compressibility data on $\mathrm{H}_{2} \mathrm{SO}_{4}$; and Stamm and Seborg do not state whether equilibrium was established by adsorption or desorption. Their published curve is,


Fig. 7.
however, better defined at high moisture contents than is Volbehr's so that the curves from these data, if less accurate, are likely to be more consistent.

Fig. 7 shows the complete system of $(p ; V)$ curves obtained. It will be noted that, with the more consistent values of $\sigma$, the sudden curvature at high vapour pressures has almost disappeared and that the curves show increasing slope, i.e. decreasing $\beta$, with increasing pressure (see footnote, * above).

If this decrease in $\beta$ is to be relied on, it disproves a tentative sug. gestion made by the author ${ }^{8}$ to account for the apparent increase in the compressibility of natural wood with increasing load. This was that the elasticity of the aggregate might be primarily governed by the vapour

[^19]pressure rather than by the moisture content. The present discussion shows the reverse to be the case, so that the apparent increase in $\beta$ with load may be due to flexibility in the anatomical structure.

Owing to uncertainties of $\mathrm{d} \sigma / \mathrm{d} m$ at humidities above about 80 per cent. and of $u$ below 30 per cent., only the average $\beta$ between these limits has been read from Fig. 7 at each moisture content, and these are
table I.-Average Compressibility of Spruce Wood-Water Aggregate.

| $h_{n} / h_{\mathrm{c}}$. | From $\sigma$ of Stamm \& Seborg ( ${ }^{\prime}$ ) ( $\left.25^{\circ} \mathrm{C}.\right)$. |  | From $\sigma$ of Volbehr ( ${ }^{(1)}\left(20^{\circ} \mathrm{C}.\right)$. |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $m$. | $\beta \times 10$. | m. | $\beta \times 10^{6}$. |
| I-O | - | - | 0.371 | 26.0 |
| 0.97 | 0.288 | 23.4 | $0 \cdot 297$ | $24^{\circ}$ |
| 0.95 | $0 \cdot 254$ | $21 \cdot 2$ | 0.268 | $22 \cdot 0$ |
| 0.90 | $0 \cdot 209$ | I9.I | 0.223 | $20 \cdot 5$ |
| -0.80 | $0 \cdot 163$ | 14.9 | $0 \cdot 171$ | I8.2 |
| 0.60 | -.II4 | $13^{\circ} \mathrm{O}$ | 0.119 | 14.5 |
| 0.40 | 0.083 | $8 \cdot 8$ | 0.085 | I2.3 |
| $0 \cdot 20$ | 0.054 | $7 \cdot 4$ | 0.054 | $8 \cdot 8$ |
| $0 \cdot 10$ | 0.035 | 7-1 | 0.035 | $7 \cdot 9$ |

given in Table. I, together with $\beta$ obtained from Volbehr's figures and the isothermal at moisture contents other than saturation. In this table $h_{n}$ refers to the natural (unstressed) vapour pressure of the aggregate.

If $\beta$ is plotted against $m$ these two sets of results are found to be in good agreement considering the limitations of the data. For the
table II.-Approximate Compressibility of Various Materials.

|  | $\begin{aligned} & \beta \times 100 \\ & \text { per bar. } \end{aligned}$ |
| :---: | :---: |
| Diamond ${ }^{\text {a }}$ | $0 \cdot 5$ |
| Aluminium ${ }^{\text {a }}$ | 1.3 |
| Quartz fibre ${ }^{\text {P }}$ | 7-1 |
| Spruce Wood-water ${ }^{\text {d }} h / h_{0}=0.15$ | $7 \cdot 3$ |
| aggregate $\int h / h_{0}= \pm .0$ | 26.0 |
| Water (at low stress) ${ }^{3(d)}$. | 50 |
| Spruce. Natural wood ${ }^{10}$ |  |
| $\left.\begin{array}{l}\text { measured on over-all } \\ \text { cross-section }\end{array}\right\} h / h_{0}=$ | $\begin{array}{r} 5 \cdot 190 \\ \cdot \quad 300 \end{array}$ |
| measured on crosssection of wood- $h / h_{0}=$ water aggregate $\int h / h_{0}=$ | . 40 | sake of comparison, Table II gives the approximate compressibilities of some other materials, including natural spruce wood.

## Applications.

When wood is prevented from swelling naturally, very high pressures may be exerted, but their magnitude cannot be deduced from the reduction in the over-all swelling because this is partially relieved internally by a reduction in size of the anatomical cell spaces. The only true criterion of internal hydrostatic stress is in the change of equilibrium moisture content in a given relative humidity. The stress is given by the intersection of the appropriate moisture content and vapour pressure lines in Fig. 7.**

Owing to the influence of species and treatment on the vapour pressure isothermal, a separate ( $p ; V$ ) diagram, obtained from controls, should be made for each type of material, but in the absence of further

[^20]data we may illustrate the use of the method by obtaining approximate values of internal stress under different conditions. The results are tabulated in Table III, where it is assumed that the presence of resin has not altered the natural hygroscopicity of the wood.

## TABLE III.

## Stresses Resulting from Constrained Swelling.

| Description. | Relative <br> Humidity $\%$. | Moisture Content <br> Deficiency \%. | Estimated <br> Pressure <br> (bars). |
| :---: | :---: | :---: | :---: |

## (1) Beech * flooring blocks clamped at zero moisture content.

| Longitudinal constraint : | $:$ | $:$ | 90 | negligible | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- |
| Radial constraint | 90 | 0.4 | Io |  |  |
| Tangential constraint $:$ | $:$ | $:$ | 90 | 90 | 0.9 |

(2) Spruce, $\dagger$ resin impregnated samples. Polymerisation without pressure.

| 33.1 | 0.43 | 100 |
| :--- | ---: | ---: |
| 54.3 | 1.25 | 130 |
| 75 | 2.05 | 160 |
| 90 | 3.56 | 115 |
| 98 | 3.20 | 50 |

(3) Beech $\ddagger$ commercial product. Polymerisation under pressure.

| Grain in all plies parallel | 60 | $1 \cdot 4$ | 350 |
| :--- | :--- | :--- | :--- |
| Grain in alternate plies perpendicular | 60 | $2 \cdot 4$ | 500 |

If the difficulty of obtaining suitable control samples can be overcome, it is probable that this method of determining internal pressures

[^21]will prove to be of importance in practical problems arising out of the manufacture of impregnated or compressed woods.

## Summary.

Making use of an empirical observation on the change of vapour pressure of solutions with pressure, as calculated by Porter's osmotic pressure equation, it has been found possible to calculate the specific volume of water in tension. Assuming that the above observation is equally applicable to hygroscopic gels, complete (pressure; volume) curves for the woodwater aggregate of sitka spruce at all moisture contents have been constructed, covering a wide range of pressures and tensions. The results are compared with those obtained on the saturated aggregate by Volbehr, who used a method of calculation which did not involve a knowledge of the vapour pressure.*

I am indebted to Mr. R. F. S. Hearmon for many of the calculations, and to Miss M. S. Smith for the illustrations. I also wish to thank the Director of the Laboratory, Mr. W. A. Robertson, for permission to publish this paper.

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[^22]
# THE ISO-ELECTRIC POINT OF GELATIN. 

By E. C. E. Hunter and A. J. Turner.

Received 28th May, 1940.
The iso-electric point of gelatin determined by a variety of physical and chemical methods lies, according to the literature, ${ }^{1}$ between pH 4.7 and pH 4.9 . Scattered observations, mainly in the technical literature, suggest that certain gelatins possess iso-electric points in the neighbourhood of $\mathrm{pH}^{7} 7$. For instance, Kraemers ${ }^{2}$ and Kraemers and Dexter ${ }^{3}$ found that the optical opacity-pH curves of certain pigskin gelatins showed maxima between pH 6 and 8 , which were ascribed to impurities in the gelatin. According to Briefer and Cohen, ${ }^{4}$ the opacity maxima found in the region pH 6.8 with certain gelatins was, in fact, due to a shift in iso-electric points. These authors state that the factor decisive in determining the $p H$ of the iso-electric point is the pH at which the precursor of gelatin, collagen in the case of animal skins, or osseine in the case of bones, is swollen (plumped), prior to extraction by water. Swelling in alkali (liming) leads to an iso-electric point of $4 \cdot 7-4.9$ while swelling in acid gives an iso-electric point nearer to pH 7.

In the preparation of gelatin from animal skins, it is necessary to remove the hairs attached to the pelt, and this is usually accomplished by treatment with aqucous alkali-lime water, caustic alkali and/or sodium sulphide, ${ }^{5}$ and the greater the degree of swelling of the skin the greater the degree of dehairing.

Modifications in or omission of the alkaline dehairing and swelling treatment are described by Briefer ${ }^{4}$ and by Sheppard and Hudsor; ${ }^{6}$ the latter remove hair by aqueous alkaline baths, to which neutral salts are added to prevent swelling. After dehairing, the skins are washed free of alkali and swollen in aqueous acid, neutralised and extracted. In a previous patent, Hudson ${ }^{7}$ used dilute acetic acid for dehairing skins and for the swelling process.

The treatment of bones for the preparation of gelatin ${ }^{5}$ may involve the removal of mineral salts by treatment with dilute acid. The demineralised "osseine" may then be treated with aqueous alkali (caustic soda or lime) for the swelling process, or the swelling is carried out in an acid medium.

No definite decision can be drawn from the literature as to the correctness of the claims for gelatin of high iso-electric points. Sheppard and

[^23]Houck ${ }^{8}$ determined the iso-electric points of gelatins prepared by the acid swelling process by $(a)$ light absorption, and ( $b$ ) alcohol precipitation, the former giving high values and the latter the normal value of $p H 4.75$. On the basis of these results the claim to a high iso-electric point was rejected. It would appear that Sheppard has revised the above statement in view of the claims of his recent patents. ${ }^{6,7}$

It will be noted that none of the above investigators determined the iso-electric points by unambiguous and absolute methods. Until data based on the determination of iso-electric points by $(a)$ chemical combinations of gelatin with ions, and (b) cataphoresis of gelatin solutions is available, no decision can be reached regarding the claims for a high iso-electric point. The purpose of the present paper is to supply unequivocal evidence based on (a) chemical combinations, and (b) electric mobilities, that certain gelatins have iso-electric points in the region pн 6.7.

The gelatins chosen for investigation are described below, and the details of their preparation were furnished by the manufacturers.

> Samples A and B-Acid swollen osseine gelatins. Samples C and D-Alkali swollen osscine gelatins. Samples E and F-Alkali swollen skin gelatins.

These samples will be referred to as "acid treated " or "limed" gelatins for brevity.

The exact details of the preparation of the above gelatins are not available.

## Experimental.

The investigations were carried out on selected gelatins de-ashed by the method of Northrup and Kunitz, ${ }^{0}$ the final operation of dialysis being continued until the pH of a $5 \%$ solution of the gelatin remained unchanged by further dialysis. Measurements of pH were made at $35^{\circ} \mathrm{C}$., using a valve potentiometer glass electrode system. All adjustments of pH measurements were


Fig. I.-Curve I. Electrometric titrations. made, using standard. acid or alkali, and. not buffer solutions.

## 1. Chemical Combination and Ionisation.

(A) Electrometric Titration Curves.$5 \%$ gelatin solutions were titrated at $35^{\circ} \mathrm{C}$. with standard acid and standard alkali. Curve I.
(B) Combination with Silver Ions and with Ferrocyanide Ions.-The methods used were essentially those of J. Loeb. ${ }^{10}$

[^24]
## 2. Dependence of Physical Properties on $\mathbf{~} \mathbf{H}$.

(A) Viscosity.-The viscosities of $5 \%$ solutions of various de-ashed gelatins were determined at $35^{\circ} \mathrm{C}$. and at various pH values obtained by adding standard HCl or standard NaOH , using a Scarpa viscometer standardised with cane


Fig. 2.-Curve II. Viscosity. sugar solutions. The results are given in centistokes. The gelatin solutions were aged for 2 hours at $35^{\circ} \mathrm{C}$. before measurements were made.
(B) Optical Opacity. -Series of tubes of o. I \% gelatin, adjusted to different $p H$ values by standard acid or standard alkali, were aged under identical conditions and allowed to stand at $15^{\circ} \mathrm{C}$. overnight. The opacities were compared visually and the $p \mathrm{H}$ of the tube of maximum opacity was measured.
(C) Swelling.-An approximate determination of the $p H$ of minimum swelling was made, using the powdered preparations.
(D) Electrophoretic Mobility.-The electrophoretic mobility was determined microscopically, using a micro-cell of rectangular cross-section


Fig. 3.-Curve III. Electrokinetic mobility of gelatin covered oil globules.
fitted with reversible copper electrodes. The migrational velocities of neutral paraffin oil globules coated with gelatine were observed at $25^{\circ} \mathrm{C}$. at a magnification of $\times 500$. The full precautions were observed as to the dimensions of the cell and the location of the stationary level. ${ }^{11}$ Abramson ${ }^{12}$ has shown that gelatin films adsorbed onto inert surfaces

[^25]behave electrokinetically as gelatin micelles, there being no denaturation, consequent on adsorption.

TABLE $I$.
Summary of Results.

| Gelatin. | Iso-Electric Point, determined by:- |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | De-Ashing. | Titration | Ion Combination. |  | Viscosity. | Opacity. | Swelling. | Electrokinetic Mobillty. |
|  |  |  | Silver | Ferrocyanide. |  |  |  |  |
| Osseine A. | $6 \cdot 25$ | 6.25 | $6 \cdot 2$ | $6 \cdot 5$ | 5-5-6.5 | $6 \cdot 2-6 \cdot 4$ | 5-5-6.5 | $6 \cdot 5$ |
| Swollen B . | $5 \cdot 9$ | $5 \cdot 9$ | $6 \cdot 1$ | $6 \cdot 5$ | 5-5-6.5 | $5 \cdot 7-6 \cdot 1$ | 5-5-6.5 | - |
| Osseine ${ }^{\text {Alkali }}$ C. | $5^{\circ}$ | $5^{\circ} 0$ | $5 \cdot 04$ | 5•I | $4 \cdot 9$ | 5.10 | $5 \cdot 0$ | - |
| Swollen (D. | 5-I | - | $5 \cdot 0$ | - | $5 \cdot 0$ | $\square$ | - | - |
| Skin ${ }_{\text {Alkali }}$ E. | 5.1 | $5 \cdot 10$ | 4.95 | 5•15 | $4 \cdot 9$ | 5.05 | $5 \cdot 0$ | $5 \cdot 05$ |
| Swollen (F. | $5 \cdot 0$ | - | 5.1 | - | $5 \cdot 0$ | - | - |  |

## Discussion of Results.

The gelatins fall into two well-defined classes.
(a) High Iso-Electric Point.-A and B acid treated.
(b) "Normal" Iso-Electric Point.-Limed osseine and skin gelatins C, D, E, F.

Samples A and B appear to be genuine gelatins in every respect, give the normal gelatin reactions, are fairly free from foreign proteins and give normal gold numbers.

The location of the iso-electric point of gelatins $A$ and $B$ was not so precise as with normal gelatins. In particular, the minimum of viscosity and swelling was a broad band of about I pH unit. The viscosity curves for gelatins A and B are almost mirror images of those for the "normal " gelatins.

It is of interest to note that the electro-kinetic mobility and titration curves for a given gelatin are approximately coincident. ${ }^{13}$ The high ph value for the iso-electric points of gelatins $A$ and $B$ is therefore caused by a difference in the basicity as compared with normal gelatins, and it must be concluded that acid swelling of osseine gives rise to a product differing in structure from that obtained by liming (alkaline swelling).

The statements of Briefer ${ }^{4}$ suggest that similar high iso-electric point gelatins are prepared from acid treated collagen, but we have not obtained samples of this type for investigation. Briefer states that commercial gelatins may be mixtures of high and normal iso-electric point gelatins, dependent on treatment in manufacture.

No value for the iso-electric point of osseine is available but values quoted for collagen by Jordan Lloyd and Shore ${ }^{14}$ range from pH 5.5 to

[^26]4.8. A recent determination of the iso-electric point of unlimed collagen ${ }^{15}$ gives a value of pri 7 . Since gelatins prepared from collagen by liming have iso-electric points about pH 5 , it would appear that greater structural changes result from liming than from acid treatment.

## Summary.

1. The iso-electric points of a series of (a) acid treated, and (b) limed gelatins, have been measured.
2. Acid treated gelatins have iso-electric points between $p_{H} 6.7$; limed gelatins iso-electric points at the normal range of $\mathrm{pH} 4 \cdot 8-5^{\circ} \%$.

The authors are indebted to the Directors of The Cassio Photographic Paper Co. Ltd. for granting permission to publish this work.

Cassio Research Laboratory, Cassio Photographic Paper Co. Lid., Walford, Herts.
${ }^{15}$ Beek and Sookne, Bur. Star. J. Res., 1939, 23, 271.

## THE EFFECT OF CERTAIN POTASSIUM SALTS ON THE ELECTROPHORETIC MOBILITY OF CETYL ACETATE EMULSIONS, AND ON THE INTERFACIAL TENSION BETWEEN CETYL ACETATE AND WATER.

By W. Dickinson.

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

Received 29th May, 1940.
The investigation of the effect of electrolytes on the electrophoretic mobility of colloidal particles dispersed in an aqueous medium has been the subject of many researches in the past. The curves relating electrophoretic mobility with salt concentration which have been reported in the literature are of a variety of types, the commonest type being that in which the mobility first rises as the salt concentration is increased, passes through a maximum at a low concentration, thereafter decreasing continuously, or decreasing to a limiting mobility as the salt concentration is increased still further. It is not proposed to discuss the significance of the maximum, but the papers of Abramson and Müller, ${ }^{1}$ Bikerman, ${ }^{2}$ and Hermans, ${ }^{3}$ may be consulted for proposed explanations of this phenomenon.

Breese and Lewis, ${ }^{4}$ investigating the effect of potassium chloride, iodide, and thiocyanate on the electrophoretic mobility of tristcarin

[^27]
## 840 ELECTROPHORETIC MOBILITY OF CETYL ACETATE

emulsions at constant $\mathrm{pH}_{\mathrm{H}}(\mathrm{pH}=4)$ obtained a " normal " type of curve with KCl in which the mobility, after passing through a maximum at a very low salt concentration, decreased with increasing salt concentration until a limiting mobility was obtained. The other two salts gave rise to a different type of curve in which the mobility first decreased as the salt concentration was increased, the mobility then passing through a minimum at a concentration of about 0.02 N ., and subsequently rose with increasing concentration of electrolyte. The rise in mobility produced by the thiocyanate was more marked than that produced by the iodide. It was suggested that this effect may be explained by the primary adsorption of thiocyanate and iodide ions at the interface, thus increasing the electrokinctic surface charge density, and the electrophoretic mobility. If this is so, the effect is presumably related to the lowering in interfacial tension, by iodides and thiocyanates, between water and an oil phase, cf. Guest and Lewis, ${ }^{5}$ and Evans. ${ }^{\text {b }}$ It therefore appears to be a matter of some interest to investigate the electrophoretic mobility of emulsions of an organic liquid in the presence of various salts, and to carry out corresponding interfacial tension measurements between the same liquid and the same salt solutions. To carry this out, it was first necessary to obtain an organic compound which would be suitable for both the electrophoretic measurements, and for the interfacial tension measurements. The compound used must give rise to stable emulsions, yielding reasonably sharp boundaries in the " U " tube, and it must be liquid at the temperature at which the investigation is carried out in order to make the measurement of interfacial tension possible. In addition, it would be a great advantage if the compound used could be easily synthesised and purified in reasonably large quantitics. After a preliminary investigation into the electrophoretic behaviour of emulsions of some organic compounds, it was decided that cetyl acetate would be a suitable compound. It was found that the mobility of emulsions of this compound in KCNS solutions was greatly different from the mobility in KCl solutions of the same concentrations. The mobility determinations were carried out at constant $\mathrm{pH}(\mathrm{pH}=4)$, because of the well-known dependence of the mobility on the pH , and the variability of the pH value of distilled water. The $p H$ value of $4^{\circ} \mathrm{O}$ could be accurately reproduced, while the pH values of unbuffered solutions of higher pH cannot be fixed with the same precision. At $p \mathrm{H} 40$, the mobility of 0.88 units ( $\mu / \mathrm{sec} . / \mathrm{v} . / \mathrm{cm}$.) is conveniently high for accurate mobility determinations to be carried out.

The next section deals with the electrophoretic measurements. This is followed by a section on the interfacial tension measurements.

## The Electrophoresis Measurements.

Experimental.-The electrophoretic mobility detcrminations were carried out by the moving boundary method, using the apparatus described by Price and Lewis. ${ }^{7}$ All the measurements were made at a temperature of $25.0^{\circ} \mathrm{C}$. by suspending the U tube in a glass trough through which water from a thermostat was circulating. The supernatant liquid was of the same ionic composition as the dispersion mixture, while to obtain the $p \mathrm{H}$ value of $4^{\circ}$, the solutions used were made $\mathrm{N} . / 10,000$ with respect to hydrochloric acid. In order to obtain sharp boundaries, $2 \%$ of A.R. sucrose

[^28]was added to the emulsion.* The $p \mathrm{H}$ values were checked from time to time by means of a glass electrode apparatus.

The Cetyl Acetate.-Cetyl alcohol (B.D.H.) was esterified in the usual way by means of acetic acid and gaseous HCl . After removing the excess acids by washing to neutrality with water, the product was dried over calcium chloride then distilled five times under reduced pressure (b.p., $188-192^{\circ} \mathrm{C}$. at 6.5 mm .), rejecting the first and last portions of each distillate. Purification was continued by recrystallisation from alcohol. After four crystallisations a product of constant interfacial tension against water was obtained, while the electrophoretic mobility of emulsions of the ester was the same as the mobility of emulsions of the ester obtained from a different source.


Fig. I.-The effect of potassium salts on the mobility of cetyl acetate and octadecyl acetate emulsions at pH 4.0 and $25^{\circ} \mathrm{C}$.

The Electrophoresis Data.-In Fig. I the mobilities are plotted against the cube-root of the concentration in order that the experimental data for the lower electrolyte concentrations may be included. It can be seen that, while the curve for KCl behaves in a " normal " manner, the curves for KI and KCNS are of a more unusual type. The curve relating the electrophoretic mobility of cetyl acetate emulsions to the concentration of KI is similar to the curves which have occasionally been obtained for the effect of NaOH on the mobility of dispersions, e.g. Ellis, ${ }^{8}$ using a hydrocarbon oil emulsion, and Roberts, ${ }^{\bullet}$ for tristearin emulsions. The KCNS curve is of a still rarer type, but a rather similar curve has been obtained

[^29]by Kruyt, Roedvoets, and van der Willigen ${ }^{10}$ for the effect of KCl on the mobility of arsenious sulphide sols. It may be noted that over the concentration range studied, the mobility in KI solutions is greater than the mobility in KCNS solutions of the same strength. This appears to imply that iodide ions are more strongly adsorbed than thiocyanate ions in this particular concentration range. If the curves are extrapolated beyond the highest salt concentration employed ( 50 millimolar), it appears that they will intersect at a concentration of about 160 millimolar, and thereafter the mobility would be greater in solutions of KCNS than in solutions of KI of the same strength.

In order to confirm the above findings, especially the rising mobility of cetyl acetate emulsions with increasing concentration of KCNS, the mobility of octadecyl acetate emulsions in solutions of KCNS and KCl has been investigated. This ester, though of similar constitution to cetyl acetate, is solid at the temperature employed $\left(25.0^{\circ} \mathrm{C}\right.$.), while cetyl acetate is liquid at this temperature. The ester used was synthesised and purified by Mr. G. C. Williams of this laboratory. The measurements were carried out at $p \mathrm{H}_{4}{ }^{\circ}$. The curves relating mobility with increasing concentrations of KCNS and of KI are similar to the corresponding curves for cetyl acetate. The curve relating mobility with concentration of KCl , after showing an unexpected minimum follows the normal course.

## The Interfacial Tension Measurements.

Experimental,-The interfacial tension measurements were carried out on the apparatus described by Matthews. ${ }^{11}$ This apparatus is a modification of the drop-volume apparatus described by Dedrick and Hanson. ${ }^{12}$ The rate of outflow of liquid from the pipette was controlled by means of a tap, the barrel of which had a $V$-notch cut into it at either end of the bore of the barrel, enabling a fine and accurate control of the rate of outflow of liquid from the pipette to be obtained. The whole apparatus was mounted rigidly in an air thermostat maintained at $25^{\circ} 0 \pm 0.05^{\circ} \mathrm{C}$. The tap was operated from the outside of the thermostat by means of a bell crank arrangement, and the extent to which the tap was opened was indicated on a scale by a pointer attached to the tap.

The apparatus was calibrated by the method described by Evans* the pipette constants obtained being similar to those obtained by Matthews.

The two phases were gently shaken and allowed to stand overnight before measurements were made in order to establish an equilibrium between them. That the two phases were in equilibrium was shown by successive determinations of the interfacial tension between cetyl acetate and the same aqueous phase giving the same value, to within the experimental error. The interfacial tension $\gamma$ is calculated by means of the equation

$$
\gamma=\frac{V\left(d_{2}-d_{1}\right) g}{2 \pi R \psi}
$$

Where $V$ is the drop volume, $d_{1}$ and $d_{2}$ are the densities of the two phases, $R$ is the radius of the tip face, $g$ the acceleration due to gravity, and $\psi$ the fraction of the ideal drop which actually falls. The values of $\psi$ were obtained from the data of Harkins and Brown. ${ }^{13}$

The densities were measured by a pyknometer of 23 ml . capacity, and were reproducible to the fourth decimal place.

A considerable saving in time was achieved by adopting an " accelerated run" technique. Instead of allowing the drops to form at a steady rate,

[^30]the drops were allowed to form rapidly until they had almost attained their full size, and then the tap was turned until the scale reading of the pointer indicated that the liquid was flowing from the pipette at a known rate. The liquid was allowed to flow at this rate until the drop detached, then the tap was opened and the process was repcated. In each run, one or two drops were allowed to form without acceleration, and the time of unaccelerated drop formation was noted.

The Effect of the Time of Unaccelerated Drop Formation and Temperature upon the Interfacial Tension between Cetyl Acetate and Water. -Harkins and Brown ${ }^{13}$ have shown that the drop volume depends to a certain extent on the rate of outflow of the liquid from the pipette at the moment the drop detaches. Using cetyl acetate as the oil phase, the dependence of the drop volume on the rate of outfow of the aqueous phase proved to be very marked. As the time of drop formation increases, the drop volume decreases, approaching a limiting value as the time of drop formation is increased indefinitcly. This limiting value was not closely approximated to until the time of unaccelerated drop formation had attained a value of thirty or forty minutes. In view of the inconvenience


Fig. 2.-The curve used for the correction of the interfacial tension data.
of carrying out interfacial tension measurements using such a slow rate of outflow of the pipette liquid it was decided to employ smaller times of drop formation and apply a correction to the interfacial tension obtained, to reduce the experimental results to those which would be obtained had a very long time of drop formation ( $>$ forty minutes) been used. The correction was obtained as follows. A series of determinations of the interfacial tension between cetyl acetate and water were carried out over an extended range of times of unaccelerated drop formation. The interfacial tension was plotted against the time taken for I c.c. of water to flow from the pipette at the rate of outfow at the moment of drop detachment; the last quantity being calculated by dividing the time of unaccelerated drop formation by the drop volume. From this curve, the correction to be subtracted from the interfacial tension corresponding to any rate of outfow of the aqueous phase could be obtained by subtracting the interfacial tension between cetyl acetate and water for an extremely slow rate of outflow from the interfacial tension corresponding to the particular rate of outflow under consideration. In Fig. 2 the correction itself has been plotted against the rate of outflow of the aqueous phase.

Assuming that the correction is merely a function of the rate of outflow of the aqueous phase, it should be the same when water is replaced by a
salt solution as the aqueous phase. The use of the correction curve may be made clearer by considering an example. Using 0.5 N. KCNS solution as the aqueous phase, a run was carried out for which the time of unaccelerated drop formation was 5 min .45 sec ., and the drop volume was $0 \cdot 1722$ c.c. From these values, it follows that the rate of outflow of the aqueous phase is 33.5 min . per c.c., and from the correction curve, it can be seen that if the aqueous phase is flowing at this rate at the moment of drop detachment, the interfacial tension obtained is $0 \cdot 15$ dynes per cm . higher than the interfacial tension which would be obtained for the same aqueous phase flowing infinitely slowly. Accordingly, $0 \cdot 15$ dynes per cm. are subtracted from the calculated interfacial tension to reduce the value to that which would be obtained for an extremely slow rate of outflow of the aqueous phase. The validity of the application of this method of correction for salt solutions has been checked on the strongest salt solutions used, I n., by measuring the interfacial tension for widely varying rates of outflow of the aqueous phase. The interfacial tensions agree closely after subtracting the necessary correction, thus appearing to justify the use of the correction curve for these solutions. For example, with n. KCl the results shown in Table I were obtained: where $T$ is the average temperature of the oil phase throughout the run,
$\boldsymbol{\gamma}^{\prime}$ is the directly obtained, uncorrected interfacial tension, given in dynes per cm.
$\gamma$ is the value of the interfacial tension obtained after correction.

TABLE 1.

| Time of Outflow of one c.c. of the Aqueous Phase in Minutes. | ${ }_{\left({ }^{\circ} \overline{\mathrm{C}}\right)}$ | $\stackrel{\gamma^{\prime}}{\text { (dynes/cm.). }}$ | (dynes/cm.). |
| :---: | :---: | :---: | :---: |
| 13.5 | $25^{\circ} \mathrm{OI}$ | 17.45 | 17.02 |
| 18.7 | 25.02 | 17.30 | 16.97 |
| $19 \cdot 2$ | 24.99 | 17.22 | 16.93 |
| $49 \cdot 4$ | 25.02 | 17.07 | 16.97 |
| 58-I | $25 \cdot 04$ | 17.09 | 16.99 |

The final column gives an idea of the magnitude of the experimental error involved in the interfacial tension determinations.

It may be mentioned that the above effect is distinct from the slow decrease with time in the surface tension of dilute solutions of capillary active substances, in which the time effect is probably due to diffusion of the solute from the bulk of the solution to the surface. In the case of the cetyl acetate-water interface, the effect depends on the rate of outflow of the aqueous phase at the moment of drop detachment, and not on the interval between successive drops which is a measure of the "age" of the surface for which the interfacial tension is taken. Runs carried out by the ordinary run technique gave the same interfacial tension as runs carried out by the accelerated run technique in which the same rate of outflow at the moment of drop detachment was adopted, but in which the interval between successive drops was greatly decreased.

It was found that the effect of temperature upon the interfacial tension between cetyl acetate and water was very marked, being 100 dynes per cm . higher at $26^{\circ} \mathrm{C}$. than at $25^{\circ} \mathrm{C}$. Because of this, it was necessary to correct the results for temperature variations, as the temperature of the oil phase can only be maintained at $25^{\circ} 0 \pm 0.05^{\circ} \mathrm{C}$. throughout the course of a run. The average value of the temperature throughout a run was found by noting the temperature to $0.0 x^{\circ} \mathrm{C}$. at the beginning of the run, after each fourth drop had fallen, and at the end of the run, and taking an average of the readings obtained. In general, there were 22 to 30 drops to a run, and from 7 to 9 thermometer readings were taken. The interfacial tension was corrected by subtracting oor dynes per cm . for each increment of $0.0 x^{\circ} \mathrm{C}$. of the average temperature above $25.0^{\circ} \mathrm{C}$.

The increase in interfacial tension with increasing temperature is presumably due to a rapid decrease in the work of adhesion between the two liquids as the temperature increases.

## The Interfacial Tension Data.

The results obtained are tabulated in Table II and illustrated in Fig. 3.

The curve representing the effect of KCl on the interfacial tension is typical of the general behaviour of electrolytes on the interfacial tension between water and an immiscible oil phase. The increase in interfacial tension with salt concentration indicates negative adsorption of the salt. Numerous attempts have been made to explain the

TABLE II.

| Salt Conc. <br> (moles/litre). | KCl <br> (dynes/cm.). | KCNS <br> (dynes/cm.). | KI <br> (dynes/cm.). |
| :---: | :---: | :---: | :---: |
|  |  | 15.89 | 15.89 |
| 0.000 | 15.89 | 15.89 |  |
| 0.005 | 15.87 | 15.86 | 15.84 |
| 0.010 | 15.88 | 15.84 | 15.57 |
| 0.020 | 15.93 | 15.75 | 15.51 |
| 0.050 | 15.94 | 15.56 | 15.27 |
| 0.100 | 15.99 | 15.37 | 15.19 |
| 0.200 | 16.09 | 14.98 | 14.93 |
| 0.500 | 16.42 | 14.13 | 14.52 |
| 1.000 | 16.98 | 13.10 | 14.19 |
|  |  |  |  | negative electrolyte adsorption, that usually accepted being due to Wagner ${ }^{14}$ or its simplified version by Onsager and Samaras ${ }^{15}$ in which the ions are supposed to be repelled from the interface by electrostatic image forces.



Fig. 3.-The effect of potassium chloride, iodide, and thiocyanate upon the interfacial tension between cetyl acetate and water.

The effects exhibited by KI and KCNS are cpposite to those of the chloride. The interfacial tension falls with increasing salt concentration, indicating positive adsorption of iodide and thiocyanate ions respectively.

[^31]If the negative ions are positively adsorbed, it is to be expected that the negative charge density at the interface will rise rapidly with increasing salt concentration. This is supported by the electrophoretic data, in which the mobility of cetyl acetate emulsions increases as the concentration of KCNS is increased over the whole concentration range studied, and the mobility increases with increasing concentrations of KI up to 2 millimolar, in spite of the simultaneously occurring diminution in the thickness of the double layer which tends to decrease the mobility. The general parallelism between the electrophoretic and interfacial tension data may be noted by comparing the curves for KI and KCNS. Both series of investigations indicate that for the lower concentrations, the iodide ion is adsorbed to a greater extent than the thiocyanate ion, and on increasing the salt concentration this order becomes reversed.

## Summary.

(I) The effect of KCl, KI, and KCNS upon the electrophoretic mobility of cetyl acetate emulsions has been investigated at constant hydrogen ion activity $\left(\mathrm{pH}=4^{\circ}\right)$, and at $25^{\circ} \mathrm{C}$.
(2) The mobility, when plotted against the concentration of KCl gives rise to a "normal" type of curve.
(3) The curves relating the mobility with the concentration of KI and KCNS, are of a more unusual type. In the case of KCNS the mobility increases over the whole concentration range studied, while the curve for KI possesses an unusually pronounced maximum.
(4) Over the concentration range investigated, the mobility in the presence of KI is greater than the mobility in the presence of KCNS solutions of the same normality, presumably indicating that iodide ions are more heavily adsorbed throughout this concentration range. On extrapolating the curves the order appears to be reversed above a concentration of about 160 millimolar.
(5) Corresponding measurements have been carried out on the effect of $\mathrm{KCl}, \mathrm{KI}$, and KCNS on the interfacial tension between cetyl acetate and water.
(6) Certain resemblances between the interfacial tension and the electrophoretic data are pointed out.

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# MAGNETISM AND VALENCY: MANGANESE COMPOUNDS. 

By N. Goldenberg.

Received 3 Ist May, 1940.
The general outline of the relation between valency and atomic structure on the one hand, and magnetic moments on the other, is to-day fairly well understood.1,2 This relation is of particular interest in the case of the co-ordination compounds of the transition elements, where recent theories ${ }^{\mathbf{3}, 4}$ indicate that their magnetic moments can yield information as to the nature of the co-ordination linkages.

Manganese is known to exhibit six valencies in its various compounds; in the present study a number of salts and co-ordination compounds of manganese have been studied, and the results obtained (together with those of other investigators) then discussed with reference to the relation between valency and magnetism. According to the quantum theory, each electron makes two contributions to the total magnetism of the compound containing it-its orbital angular momentum and its spin angular momentum. Their algebraic sum is the resultant magnetic moment of the compound. Atoms or ions which contain completed sub-groups are either diamagnetic or very feebly paramagnetic, whilst those with incomplete subgroups are truly paramagnetic. It is theoretically possible, however, for an atom with an even number of electrons in

TABLE I.

| Valency of Ion. | No. of Unpaired Electrons. | Magnetic Moment. |
| :---: | :---: | :---: |
| Univalent $\mathrm{Mn}^{1}$ | 6 | $6 \cdot 93$ |
| Divalent Mn ${ }^{\text {2 }}$ | 5 | $5 \cdot 92$ |
| Tervalent Mn ${ }^{3}$. | 4 | $4 \cdot 90$ |
| Tetravalent Mn ${ }^{\text {c }}$ | 3 | $3 \cdot 87$ |
| Hexavalent Mn | 1 | -73 |
| Heptavalent Mn ${ }^{\text {? }}$ | 0 | $\bigcirc$ | an incompletely filled subgroup to be diamagnetic. ${ }^{5}$ It is now known ${ }^{8}$ that the orbital angular component is completely "quenched " by interatomic forces for most of the compounds formed by the elements of the iron group. It can then be calculated that the magnetic moment $\mu$ in Bohr units would be

$$
\begin{equation*}
\mu=\sqrt{4} \overline{S(S+I)} . \tag{I}
\end{equation*}
$$

where $S=\Sigma s$, and $s=\frac{1}{2}$ for each unpaired electron.
It is then possible to calculate from equation (I) the theoretical magnetic moments of the various ions of manganese (see Table I).

For co-ordination compounds, it has been suggested that not only the unpaired electrons of the paramagnetic ion should be taken into

[^32]account, but also those which are "donated " to it by the co-ordinated groups. This hypothesis accounted satisfactorily for some of the results obtained (e.g. with cyanide complexes), but failed with others. It was then shown by Pauling ${ }^{3}$ that it was necessary to distinguish between the different kinds of chemical bonds occurring in co-ordination compounds, viz. : (a) ion dipole bonds, $(b)$ ionic bonds, and ( $c$ ) electron pair bonds. The last were equivalent in the final result to a transfer of an electron from the donor (the co-ordinating group) to the acceptor (the paramagnetic ion). Pauling suggested that with the first two types of bond, co-ordination would not affect the effective magnetic moment but the third type would do so, the change being dependent on the number of co-ordinating groups and the valency of the acceptor. On this basis the magnetic moments of the co-ordination compounds of manganese would be as in Table II.

The experimental methods employed to determine the atomic mass susceptibility $\chi_{a}$, and hence the magnetic moment $\mu$, have already been described in detail. ${ }^{5}$ The results obtained, together with those of other investigators, are summarised in Table III. The columns headed $\chi$ and $\chi_{m}$ give the measured susceptibility per g. and per g.-mol, respectively,

TABLE II.

and $\delta$ is the correction for the diamagnetism of the atoms or radicles attached to the manganese atom.

Before correlating the results presented in Table III with the foregoing theory, it is necessary to make two observations, which are more connected with the experimental than the theoretical side of the work. Firstly, many of the salts were investigated only at one temperature, and the Curie law $\chi T=C$ then used to calculate $\mu$. This procedure (also followed in the present study), assumes that in the more generally applicable Weiss law $\chi(T-\theta)=C, \theta$ was very small or zero. There are indications, however, ${ }^{36}, 16,18,25,15$ that $\theta$ may have a definite though small value in many " magnetically dilute" manganese salts. Some of the smaller deviations from theory listed above may thus be due to this cause. Manganic phosphate (No. 23) offers a good example of this. The results obtained by the author, assuming the applicability of the Curie law, were low compared with theory ( $\mu=4 \cdot 49$, instead of 4.90 ). It was, however, shown by Birckel ${ }^{18}$ that this substance followed only the Weiss law, with $\theta=-53$. On recalculating $\mu$ on this basis, a figure of 4.89 was obtained, in excellent agreement with theory, and with Birckel's value of 4.92 (No. 24).

In the second place, it should be pointed out that few of the magnetic measurements on manganese compounds reported in the literature were

TABLE III.


Effective Ion Mn ${ }^{4}$.


## Effective Ion Mns.

| $\mathrm{NH}_{4}\left[\begin{array}{c}\left.\mathrm{C}_{6} \mathrm{H}_{4} \cdot \mathrm{O} . \mathrm{COO}\right)_{2} \\ \mathrm{Mn} 2 \mathrm{H}_{2} \mathrm{O}\end{array}\right] 2 \mathrm{H}_{2} \mathrm{O}$ | Author | 17.5 | 23.35 | 9740 | -200 | 4.81 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{K}_{4}\left[\mathrm{Mn}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)\right] 3 \mathrm{H}_{2} \mathrm{O}$. | Author | I $8 \cdot 0$ | 19.98 | 9793 | - 123 | 4.81 |
| $\mathrm{K}_{3}\left[\mathrm{Mn}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)\right]_{3} \mathrm{H}_{2} \mathrm{O}$ | Wis | 20 |  | 10470 |  | 4.96 |
| $\mathrm{K}_{9}\left[\mathrm{Mn}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)\right]_{3} \mathrm{H}_{2} \mathrm{O}$ | $\mathrm{J}^{18}$ |  |  |  |  | 4.88 |
| $\left.\mathrm{Ma}^{\left(C \mathrm{CH}_{3}\right.} \cdot \mathrm{COO}\right)_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ | Author | $18 \cdot 2$ | $36 \cdot 16$ | 9690 | - 116 | 4.78 |
| $\mathrm{Mn}\left(\mathrm{CH}_{3} \cdot \mathrm{COO}\right)_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ | DS ${ }^{18}$ |  |  |  |  | 4.94 |
| $\dagger \mathrm{MnPO}_{4}$. | We ${ }^{17}$ |  |  | 10840 |  | $5 \cdot 04$ |
| $\dagger \mathrm{Mn}_{2}\left(\mathrm{SO}_{4}\right)_{3}$ | We ${ }^{17}$ |  |  | 11500 |  | 5.19 |
| $+\mathrm{MnCl}_{3}$. | We ${ }^{17}$ |  |  | 10900 |  | 5.08 |
| $\mathrm{MnPO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$ | Author | 16.7 | 5I.48 | 8645 | - 60 | 4.49 |
| $\mathrm{MnPO}, \mathrm{H}_{2} \mathrm{O}$ | $\mathrm{B}^{18}$ | - I80-20 |  |  |  | 4.92 |
| $\mathrm{MnNH} \mathrm{S}_{2} \mathrm{O}_{7}$ | $\mathrm{B}^{18}$ | - 180-20 |  |  |  | 4.88 |
| $\mathrm{Mn}\left(\mathrm{CH}_{3}, \mathrm{CO}, \mathrm{CH}_{2}, \mathrm{COCH}_{2}\right)_{3}$ | $\mathrm{Ja}^{10}$ | -257-19 |  |  |  | 4.98 |
| $\mathrm{K}_{3} \mathrm{Mn}(\mathrm{CN})_{8}$. . . | Author | 19.1 | 13.48 | 4423 | -100 | 3.25 |
| $\mathrm{K}_{8} \mathrm{Mn}(\mathrm{CN})_{8}$. | $B i^{20}$ | $19 \cdot 0$ | 16.7 | 5478 | -100 | $3 \cdot 61$ |
| $\mathrm{K}_{3} \mathrm{Mn}(\mathrm{CN})_{0}$. | $\mathrm{RB}^{21}$ | $25^{\circ}$ | 10.8 | 3543 | - 100 | $2 \cdot 95$ |
| $\mathrm{K}_{3} \mathrm{Mn}(\mathrm{CN})^{8}$ | $\mathrm{SO}^{22}$ |  | 14.8 | 4980 | -100 | 3.40 |
| $\mathrm{K}_{3} \mathrm{Mn}_{2}(\mathrm{CN})_{9} \cdot 4 \mathrm{KOH}$ | Author | 18.5 | -0.7 | -49 | -167 | 0.62 |
| $\mathrm{Mn}\left(\mathrm{C}_{5} \mathrm{H}_{7} \mathrm{O}_{2}\right)_{3}$ | $\mathrm{CS}^{23}$ |  | $28 \cdot 6$ | 10226 |  | $4 \cdot 86$ |
| $\mathrm{Mn}\left(\mathrm{C}_{16} \mathrm{H}_{14} \mathrm{~N} \cdot \mathrm{CS}_{2}\right)_{3}$ | $\mathrm{CS}^{23}$ |  | 12.0 | 10957 |  | 5.02 |
| $\mathrm{Mn}\left(\mathrm{C}_{5} \mathrm{H}_{10} \mathrm{~N} . \mathrm{CS}_{2}\right)_{3}$ | $\mathrm{CS}^{23}$ |  | 18.8 | 103II |  | 4.88 |
| $\mathrm{Mn}\left(\mathrm{C}_{8} \mathrm{H}_{18} \mathrm{~N} . \mathrm{CS}_{2}\right)_{3}$ | $\mathrm{CS}^{23}$ |  | 14.1 | 9834 |  | $4 \cdot 76$ |

[^33]TABLE III (Continued).


[^34]accompanied by accurate analyses, and it is possible that some of the smaller deviations from theory are due to this cause. The value of such analyses is well illustrated in the case of $\mathrm{BaMnO}_{4}$. The material prepared did not appear to differ from the product described in the literature, but on analysis two separate preparations were found to contain only $50-60 \% \mathrm{BaMnO}_{4}$; when corrected for this, the value for $\mu$ agreed well enough with theory (No. 8). Wedekind's preparation (No. 7), which gave a much higher value, may have been contaminated by a small amount of the highly magnetic oxides of manganese. Wedekind's $\mathrm{BaMnO}_{4}$ was prepared by the action of $\mathrm{H}_{2} \mathrm{O}_{2}$ on a solution of $\mathrm{KMnO}_{4}$ made alkaline with $\mathrm{Ba}(\mathrm{OH})_{2}$; these conditions appear to be favourable for the formation of manganese oxides, which would account for the high value for $\mu$. Similarly, a small quantity of $\mathrm{MnO}_{2}$ was found to be present in the double sait of potassium and tetravalent Mn (No. II) and had to be aliowed for (see experimental section). The corrected value agreed well with theory.

If the discrepancies due to the above two causes be allowed for, the tabulated results show that whether the Mn is present as an ionisable cation, or as part of a large anion, the values of $\mu$ agree quite well with those predicted by theory, with the exception only of those compounds

TABLE IV.

| Compound. | Eff. | Unpaired Electrons in Ion. | Observed. | Predicted by Theory. | Unpaired Electrons left in cpd . |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{K}_{3} \mathrm{Mn}(\mathrm{CN})_{8}$ | $\mathrm{Mn}^{3}$ | 4 | 3.25 | $2 \cdot 83$ | 2 |
| $\mathrm{K}_{3} \mathrm{Mn}_{2}(\mathrm{CN})_{9} .4 \mathrm{KOH}$ | $\mathrm{Mn}^{3}$ | 4 | 0.00 |  | - |
| $\mathrm{K} M \mathrm{Mn}(\mathrm{CN})_{8} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ | $\mathrm{Mn}^{2}$ | 5 | $2 \cdot 13$ | 1.73 | 1 |
| $\mathrm{KMn}(\mathrm{CN})_{3}$. | $\mathrm{Mn}^{2}$ | 5 | 4.22 | 3.87 | 3 |
| $\mathrm{K}_{5} \mathrm{Mn}(\mathrm{CN})$ 。 | $\mathrm{Mn}^{1}$ | 6 | 0.00 | $0 \cdot 00$ | 0 |

where the CN group is co-ordinated to the Mn in the anion. It is to be presumed, therefore, if Pauling's theories of the nature of the chemical bond be accepted, that (so far as manganese is concerned), the only electron-pair bonds formed with it are to be found in its complex double cyanides. In view of this, their magnetic moments have been collected in Table IV and compared with those predicted on the basis of electron-pair bond formation.

The value for $\chi_{m}$ obtained in the present investigation for the univalent double cyanide is much smaller than that found by Bhatnagar et al. (No. 68), and it is suggested that the latter may be due to the greater degree of oxidation suffered by their preparation because of its greater exposure to air. The actual value obtained indicates the presence of a small residual paramagnetism, but the magnetic moment is essentially zero.

[^35]Values for $\mu$ for the anions $\left[\mathrm{Mn}_{2}(\mathrm{CN})_{9}\right]^{\prime \prime \prime}$ and $\left[\mathrm{Mn}(\mathrm{CN})_{3}\right]^{\prime}$ were not worked out by Pauling ; the compound $\mathrm{KMn}(\mathrm{CN})_{3}$ has, however, been suggested to be a "supercomplex" co-ordination compound ${ }^{37}$ of the formula $\mathrm{K}_{2}\left[\mathrm{Mn}\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]\right]$. On this basis, the $\mathrm{Mn}(\mathrm{CN})_{6}$ group would have one unpaired electron as in $\mathrm{K}_{4} \mathrm{MN}(\mathrm{CN})_{8}$ and the entire compound would then have six unpaired electrons per double molecule, in agreement with the observed result. The agreement between theory and experiment in Table IV is thus fairly good; it should be pointed out that the differences between the predicted and the observed values for $\mu$ may be due to incompletely "quenched" orbital contributions ( $c f$. Van Vleck ${ }^{4}$ ). In terms of the electronic theory of valency, some of the electrons in the uncompleted subgroup of the Mn in the double cyanides have paired up, and the orbits so made available have been used for the direct covalent binding of the co-ordinated CN groups. In the other complex compounds of Mn so far investigated, this does not occur, and the binding forces must therefore be regarded as mostly or entirely electrostatic in character.

This survey of the magnetism of the compounds of manganese would be incomplete without mentioning those compounds which are not "magnetically dilute." This class comprises the various oxides and sulphides of $\mathrm{Mn}, \mathrm{MnSe}, \mathrm{MnTe}$, etc. Here the constant $\theta$ of the Weiss
 consideration in calculating $\mu$, the results obtained generally agree quite well with those given by the "spin only" formula (equation (I)). Finally, a number of compounds such as $\mathrm{MnAs}, \mathrm{MnSi}_{2}, \mathrm{MnSi}, \mathrm{Mn}_{2} \mathrm{Si}$, etc., appear to have magnetic properties which indicate the presence of non-ionised Mn. ${ }^{45}$

## Experimental.

Determination of Magnetic Susceptibilities.-The method used was that described by Sugden, ${ }^{\text {b }}$ except that the glass tube carrying the substance to be measured was used without the outer tube referred to in the above paper.

Preparation of Materials. $-\mathrm{KMn}(\mathrm{CN})_{3}$ and $\mathrm{K}_{3} \mathrm{Mn}(\mathrm{CN})_{6} \cdot \mathrm{H}_{2} \mathrm{O}$ were prepared as described by Christensen. ${ }^{45}$ The former (Mn found $32.03 \%$; calc. $31.98 \%$ ), could be kept indefinitely over conc. sulphuric acid in vacuo, but the latter was very susceptible to atmospheric oxidation, and it was therefore very necessary to measure its magnetism as rapidly as possible. The salt was dried as completely as possible by pressing it between filter papers, some weighed on for analysis, and the magnetism immediately measured (Mn found $12.30 \%$; calc. $13.07 \%$ ). The discrepancy in Mn content was doubtless due to the imperfect drying, and the magnetic moment corrected accordingly. The double oxalate

$$
\mathrm{K}_{2} \mathrm{Mn}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}
$$

was prepared from manganous oxalate and neutral potassium oxalate. ${ }^{68}$ Mn found $16.36 \%$; calc. $15.94 \%$. The magnetic moment was calculated on the actual Mn content. The manganic acetate $\mathrm{Mn}\left(\mathrm{CH}_{3}, \mathrm{COO}\right)_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ was prepared from dry $\mathrm{Mn}_{3} \mathrm{O}_{4}$ and glacial acetic acid, ${ }^{47}$ and was obtained as reddish-yellow lumps, which were crushed up and dried between filter papers, and stood over CaO in vacuo till free from acetic acid. Mn found $20.58 \%$; calc. $20.53 \%$. Manganic phosphate $\mathrm{MnPO}_{4} . \mathrm{H}_{8} \mathrm{O}$ was obtained by Christensen's method " (Mn found $32.55 \%$; calc. $32.75 \%$ ), and was then used to obtain $\mathrm{K}_{3} \mathrm{Mn}(\mathrm{CN})_{0}$, which was obtained ${ }^{42}$ in the form of deep reddish-golden needles. Mn found $16.80 \%$; calc. $16.77 \%$. The double oxalate of tervalent manganese, $\mathrm{K}_{3} \mathrm{Mn}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3} \cdot-3 \mathrm{H}_{2} \mathrm{O}$ was
prepared by Souchay and Lensson's method. ${ }^{50}$ On account of its instability, it was only dried between filter papers, and then its magnetism measured immediately. Mn found $10 \cdot 66 \%$ cals. II $23 \%$. The difference was doubtless due to the imperfect drying, and the magnetic moment corrected accordingly. $\left[\begin{array}{cr}\left(\mathrm{C}_{6} \mathrm{H}_{4} \cdot \mathrm{O} \cdot \mathrm{COO}\right) \\ 2 \mathrm{H}_{2} \mathrm{O}\end{array} \mathrm{NH}_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}\right.$ was prepared according to Barbieri's method. ${ }^{11}$ Mn found $12.42 \%$; calc. $13.17 \%$. The magnetic moment was corrected for the low Mn content.

The compound $\mathrm{K}_{3} \mathrm{Mn}_{2}(\mathrm{CN})_{9} \cdot 4 \mathrm{KOH}$ was obtained in the course of an unsuccessful attempt to prepare a double cyanide of tetravalent Mn, $\mathrm{K}_{4} \mathrm{Mn}(\mathrm{CN})_{8}$, reported by Yakimach. ${ }^{62}$ This was supposed to be prepared from saturated aqueous $\mathrm{KMnO}_{4}$ (approx. $6.7 \%$ ), and a solution containing 80 g . KCN to 100 g . water. When the recommended quantities were used, a bulky ppt. of $\mathrm{MnO}_{2}$ resulted, and the remaining yellow solution gave no further products on standing. Preliminary experiments then showed that when 4 c.c. of the sat. $\mathrm{KMnO}_{4}$ solution were used with 5 c.c. of the KCN solution some brown crystals were obtained. Mn found $15.54 \%$; calc. for $\mathrm{K}_{4} \mathrm{Mn}(\mathrm{CN})_{8}-13 \cdot 15 \%$. The crystals were diamagnetic. A large scale preparation was thereupon carried out, in which $212.5 \mathrm{c} . \mathrm{c}$. of the permanganate solution were added drop by drop to 250 c.c. of the KCN solution, contained in a beaker cooled in ice. On completion, the mixture was filtered, the filtrate allowed to stand, and re-filtered every twenty-fourhours. During the first twenty-four hours a mixture of $\mathrm{MnO}_{1}$ and some golden crystals precipitated out; in the second twenty-four hours 5 g . of apparently pure golden crystalline plates were obtained, and further small quantities of these crystals were filtered off from time to time. The second crop gave the following results on analysis: $\mathrm{Mn} 15.83 \%$; CN $34.38 \%$; K $40.53 \%$. Calc. for $\mathrm{K}_{4} \operatorname{Mn}(\mathrm{CN})_{8}$ : Mn 13.15 \% ; CN $49.16 \%$ and $\mathrm{K} 37.6 \%$. To settle the valency of the manganese present, the $\%$ active oxygen was determined by dissolving a weighed quantity in standard oxalic acid, and back-titrating with standard permanganate, and the $\%$ active oxygen found was $2.08 \%$, in fair agreement with the value for trivalent Mn, $2.34 \%$. The tentative formula $\mathrm{K}_{3} \mathrm{Mn}_{8}(\mathrm{CN})_{9} .4 \mathrm{KOH}$ was therefore assigned to the complex, which was found to be diamagnetic.
$\mathrm{K}_{2} \mathrm{Mn}\left(\mathrm{IO}_{3}\right)_{\text {, }}$ was prepared by Berg's method ${ }^{\text {s3 }}$ from freshly made $\mathrm{MnO}_{2}$, iodic acid and $\mathrm{KIO}_{3}$. Its Mn content was $7.98 \%$ (calc. $4.65 \%$ ). This result was in accordance with the literature, which states that the double salt was always contaminated with some $\mathrm{MnO}_{2}$, probably obtained by hydrolysis during washing. On this basis, the material was composed of $5 \% \% \mathrm{MnO}_{3}$ and $94.3 \%$ of the double salt, and the magnetic moment corrected accordingly. $x$ for $\mathrm{MnO}_{2}$ was taken to be $46 \cdot 58$. BaMnO ${ }_{4}$ was prepared from solutions of $\mathrm{K}_{2} \mathrm{MnO}_{4}$; the latter being made by fusing together $\mathrm{MnO}_{2}, \mathrm{KClO}_{3}$, and NaOH according to Moissan's method. Prepared in this way the barium manganate was very impure ( Mn found $12.64 \%$; calc. $21.45 \%$. Ba found $42.1 \%$; calc. $53.6 \%$ ). The impurities were concluded to be $\mathrm{BaCO}_{8}$ and a little water, and the magnetic moment was calculated on the actual Mn content.

The univalent double cyanide was prepared by Manchot's method, ${ }^{\text {ss }}$ using very finely divided aluminium paint powder to carry out the reduction. Washing and handling operations were reduced to a minimum, as the white preparation obtained immediately formed a blue skin on its surface on the least exposure to air. Quantities were weighed on for analysis, and the magnetism measured immediately. In the original paper much more washing was advocated, but this was found impracticable in view of the slow filtration, and the consequent risk of oxidation. Found, Mn $10.57 \%$, CN $33.95 \%$; calculated for $\mathrm{K}_{5} \mathrm{Mn}(\mathrm{CN})_{8} \mathrm{Mn}$ I3.55, \% CN $38.43 \%$. The insufficient washing and incomplete drying doubtless accounted for the presence of excess KCN and water. The magnetic moment was therefore calculated on the actual Mn content.

Methods of Analysis.-Manganese was determined as

$$
\mathrm{NH}_{4} \mathrm{MnPO}_{4} \cdot \mathrm{H}_{2} \mathrm{O},
$$

the precipitation being carried out under carefully controlled conditions. ${ }^{55}$ CN was determined by the Liebig-Deniges method. The $\mathrm{MnNH}_{4} \mathrm{PO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$ was afterwards used for magnetic measurements.

## Summary.

A comprehensive survey has been made of the literature dealing with the magnetic moments of the simple and complex salts of manganese; the magnetic moments of thirteen salts, mostly complex, have been measured.

With the exception of the complex cyanides, the magnetic moments of the manganese salts so far measured, are almost exactly those of the manganese ions present, indicating that the linkages concerned are electrostatic in nature. The magnetic moments of the double cyanides agree well enough with those forecast by Pauling, and indicate direct covalent binding of the co-ordinated CN groups.

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## ON THE ENERGY AND ENTROPY OF LIQUID SURFACES.

By H. Campbell and D. D. Eley.

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The surface tension $\gamma$ in dynes per cm . gives the change in Gibbs function $\Delta G$ in ergs when the surface of a mass of liquid is increased by I square centimetre. Then

$$
\begin{aligned}
\Delta S & =-\left(\frac{\partial \gamma}{\partial T}\right)_{p} \\
\Delta E \sim \Delta H & =\gamma-T\left(\frac{\partial \gamma}{\partial T}\right)_{p}
\end{aligned}
$$

and
In this note we are interested in the molar surface energy and entropy, which cannot be defined in an exact fashion. We employ as an approximate measure of the molar surface free energy, the expression $\mu=\gamma\left(\frac{M}{\rho}\right)^{\frac{z}{2}}$, as in the well-known Eötvos equation. It may reasonably be taken as giving relative values of this free energy over a series of liquids, when they have approximately spherical molecules and in the absence of orientational effects in the surface. The molar quantities are then

$$
\begin{aligned}
& \Delta S_{\text {molar }}=-\left(\frac{\partial \mu}{\partial T}\right)_{p}=-\left(\frac{\partial \gamma}{\partial T}\right)_{p}\left(\frac{M}{\rho}\right)^{\frac{z}{2}}+\frac{2}{3} \gamma\left(\frac{M}{\rho}\right)^{\frac{z}{2}} \frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{p} \\
& \Delta E_{\text {molar }}=\mu-T\left(\frac{\partial \mu}{\partial T}\right)_{p}
\end{aligned}
$$

Recently Evans and Polanyi ${ }^{1}$ have shown that there exists a linear relationship between the heats and entropies of solution of a solid solute in a series of solvents, in a number of cases. Bell has demonstrated such a relationship for a series of gases in a particular solvent. ${ }^{2}$ Barclay and Butler have further shown a similar approximate relationship for the vaporisation of pure liquids. ${ }^{3}$ It can be seen from the figure in which


Fig. . .*
we have plotted $T \Delta S_{\text {molar }}$ against $\Delta E_{\text {molar }}$, as defined above, that such a relationship holds for the formation of liquid surfaces to about the same accuracy as it does for the last-named case. ${ }^{3}$ The points are calculated from measurements of $\gamma,\left(\frac{\partial \gamma}{\partial T}\right)_{D}, \rho$ and $\left(\frac{\partial \rho}{\partial T}\right)_{D}$ made at $25^{\circ} \mathrm{C}$. The large majority of them are by Timmermans and Hennaut-Roland, ${ }^{4}$ together with a few values at the extremities of the graph by Jaeger. ${ }^{5}$ It is
${ }^{1}$ Evans and Polanyi, Trans. Faraday Soc., 1936, 32, 1333.
${ }^{2}$ Bell, ibid., 1937, 33. 496. ${ }^{3}$ Barclay and Butler, ibid., 1938, 34, 445.
${ }^{4}$ Timmermans and Hennaut-Roland, J. Chim. Physique, 1930, 27, 401; 1932. 29, 529.
${ }^{5}$ Jaeger, Z. anorg. Chem., 1917, 10I. I.

## Timmermans and Hennaut-Roland.

x. m-xylene.
2. $n$-propylbenzene.
3. Tetrachlorethylene.
4. n-propyl chloride.
5. n-butyl chloride.
6. o-chlortoluene.
7. Methyl alcohol.
9. n-dipropyl ether.
ro. $n$-dibutyl ether.
II. Acetic anyhdride.
12. Formic acid.
13. Acetic acid.
14. Propionic acid.

I6. Ethyl acetate.
17. Ethyl propionate.

IS. Ethyl carbonate.
19. Ethyl oxalate.
20. Acetonitrite.
21. Di-isobutyl.
22. Methylene dichloride.
25. Allyl chloride.
27. n-amyl alcohol.
28. Dimethyl ethyl carbinol.
29. Diethyl carbinol.
30. Methyl n. propyl carbinol.
31. Allyl alcohol.
33. n-butyric acid.
34. $n$-valerianic acid.
35. Isovaleric acid.
36. Ethyl formate.
37. $n$-ethyl butyrate.
38. Triethylamine.
39. Nitromethane.
40. Allyl thiocyanate.

Jaeger.
A. Water.
B. Ethyl alcohol.
C. Isobutyl alcohol.
D. Ethyl propyl-acetyl-acetate.
E. Diethyl malonate.
F. Diethyl brommalonate.
significant that if the $\gamma$ quantities instead of the $\mu$ quantities be used, no such relationship is obtained; such relationships are only to be expected for molar quantities. A part of the deviations from the straight line may be due to the inadequacy of $\mu$ as a measure of the relative molar surface free energy. That a part may also reside in the experimental error is shown by the fact that a plot of all the earlier, less accurate, values of Jaeger shows a greater spread still.

The quantity - $(\partial \mu / \partial T)_{\mathcal{D}}$ is Eötvos' "constant," low values of which were classically attributed to association, so that the value of $M$ should actually be higher than the formula weight used in the equation. It is now apparent that many deviations in this "constant" form a part of the more general energy-entropy relationships holding over a considerable range of liquid phenomena. There are, however, specific deviations which do not enter into this relationship, such as those for liquid crystals, where the fact that the molecules are highly ordered in the interior of the anisotropic liquid results in an abnormally high value of $-(\partial \mu / \partial T)_{p}$. There has been as yet no satisfactory theory of these energy-entropy relationships, although Bell ${ }^{2}$ has indicated how they might arise for solubility.

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## THE INTERACTION OF OH RADICALS AND OF SIMILAR FREE RADICALS.

By Joseph Weiss.
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## 1.

Free radicals are formed in comparatively high concentrations in many reactions in the gaseous phase and in solution, so that, apart from their reactions with the other molecules present, the interaction of the radicals themselves assumes a more important aspect.

Two radicals will often recombine to give the corresponding dimer, as is usually the case with free atoms forming diatomic molecules. These simple recombination reactions with atoms can occur only by ternary collisions, and this is also true in general at least for the association of simple radicals. It would be expected, therefore, that the reaction of radicals $R$ according to ( $I$ )

$$
\begin{equation*}
\mathrm{R} \cdot+\mathrm{R} \cdot+(\mathrm{M})=\mathrm{R}: \mathrm{R}+(\mathrm{M}) \tag{I}
\end{equation*}
$$

would generally be favoured in solutions, where a third body (M) is practically always present, but not in the gaseous state at ordinary pressures.

The other alternative is represented by the dismutation reaction whereby an electron or a hydrogen atom (from radicals of the type RH ) is transferred and two saturated molecular species are formed:

$$
\begin{align*}
\mathrm{R} \cdot+\mathrm{R} \cdot & =\mathrm{R}:+\mathrm{R},  \tag{2a}\\
\mathrm{RH}+\mathrm{RH} & =\mathrm{RH}_{2}+\mathrm{R} . \tag{2b}
\end{align*}
$$

In practice it is found with many radicals with a strong permanent dipole moment that dismutation is favoured rather than recombination in the gaseous phase and in solution.

For non-polar radicals, e.g. $\mathrm{CH}_{3}, \mathrm{C}_{6} \mathrm{H}_{5}$, dimerisation can occur, in general as a ternary collision, such as :

$$
\begin{equation*}
2 \mathrm{CH}_{3}+(\mathrm{M})=\mathrm{C}_{2} \mathrm{H}_{6}+(\mathrm{M}) . \tag{3}
\end{equation*}
$$

In the case of radicals with a permanent dipole moment the following has to be borne in mind. Consider, for instance, the OH radical which possesses a strong dipole moment with the negative end on the oxygen. If two OH radicals were to recombine to give an $\mathrm{H}_{2} \mathrm{O}_{2}$ molecule the two oppositely charged ends of the molecular dipoles would have to approach each other to a distance such that the valency forces could come into play to form the new bond. The valency energy falls off exponentially $\left(\sim e^{-\frac{\gamma}{a}}\right)$, whereas the potential energy of two dipoles falls off with the third power of the distance $r$. This energy of repulsion $E_{r}$ which will act as an activation energy has to be overcome before the $\mathrm{H}_{2} \mathrm{O}_{2}$ molecule can be formed.
$E_{\mathrm{T}}$ can be estimated roughly for the above case $E_{\mathrm{r}} \sim \mu^{2}{ }_{\mathrm{OH}} / r^{3} \sim 4.6$ k.cal., for $\mu_{\mathrm{OH}}=\mathrm{I} .66 \mathrm{D}$ (group moment of OH ) and $r \sim 2 \mathrm{~A}$, the $\mathrm{O}-\mathrm{O}$ distance in $\mathrm{H}_{2} \mathrm{O}_{2}$ being $\mathrm{I} \cdot 4$ A. ${ }^{1}$ This is a comparatively low activation energy, so that a fairly fast reaction should be possible even at room temperature.

There is, however, still another point, with regard to the dynamical behaviour of dipole radicals: this will depend mainly on the shape of the radicals and on the magnitude and position of the electric moment within the radical. In a random distribution there is an equal probability for the positions of attraction and repulsion. However, if the dipole radicals approach, they exert a couple on each other, so that the positions of attraction are favoured compared with the positions of repulsion. The dipole radicals will assume the position of lowest potential energy (small total electric moment), so that configuration (a). is generally favoured rather than configuration (b) (Fig. I).

(a)

(b)
Fig. 1.

Therefore, for dipole radicals, if a dismutation is possible, it will always be favoured rather than recombination. It will, of course, also strongly depend on the activation energy of the dismutation reaction in question. If only a hydrogen atom or an electron has to be transferred to form two saturated molecules this activation energy will generally be small.

For the OH radicals the reaction can be represented as in Fig. 2 :

[^36]The above dismutation reaction should have an exceedingly small heat of activation, because very little motion of the atoms is necessary to pass from the original to the final position where the new bond is formed. On the simple picture given above only a change of the valency angle (from $90^{\circ}$ to $110^{\circ}$ ) is necessary, and the rearrangement requires only small changes in the electronic configuration. ${ }^{2}$

In agreement with the above consideration Bonhoeffer and Pearson ${ }^{3}$ lave represented the reaction of OH radicals in the gaseous phase as :

$$
\begin{equation*}
2 \mathrm{OH}=\mathrm{H}_{2} \mathrm{O}+\mathrm{O} . \tag{4}
\end{equation*}
$$

Similarly, the reaction between the polar SH radicals yields ${ }^{4}$

$$
\begin{equation*}
2 \mathrm{SH}=\mathrm{H}_{2} \mathrm{~S}+\mathrm{S} . \tag{5}
\end{equation*}
$$

The radical $\mathrm{HSO}_{3}$, which appears in the oxidation of sulphite solutions, yields only very small quantities of dithionic acid $\mathrm{H}_{2} \mathrm{~S}_{2} \mathrm{O}_{6}$ but undergoes a dismutation ${ }^{5}$

$$
\begin{equation*}
2 \mathrm{HSO}_{3}=\mathrm{H}_{2} \mathrm{SO}_{3}+\mathrm{SO}_{3} . \tag{6}
\end{equation*}
$$

The same is also true for the $\mathrm{HO}_{2}$ radicals, which show a dismutation according to ${ }^{6}$

2.

The interaction of these radicals can clearly be studied in the following manner.

OH radicals are formed from $\mathrm{H}_{2} \mathrm{O}_{2}$ by irradiation in the ultraviolet, thus: ${ }^{\text {? }}$

$$
\mathrm{H}_{2} \mathrm{O}_{2}+h \nu=2 \mathrm{OH} .
$$

The radicals so formed should interact according to reaction (4), which would eventually give water and molecular oxygen through the recombination of the O atoms. However, the quantum efficiency of the photochemical decomposition of $\mathrm{H}_{2} \mathrm{O}_{2}$ is considerably greater than unity. We know that this is due to the OH radicals reacting with $\mathrm{H}_{2} \mathrm{O}_{2}$ molecules generating a more complicated chain reaction. ${ }^{8}$ Therefore the mechanism discussed above cannot be tested in this particular case.

However, this mechanism can be demonstrated in the case of het photochemical decomposition of hydrazobenzene, recently studied in this laboratory. On irradiating an alcoholic solution of hydrazobenzene in the region between 2300-2700 A, in the absence of $\mathrm{O}_{2}$, aniline and azo-

[^37]benzene are obtained, without the formation of any gas, with a quantum efficiency smaller than unity.

In the experiments a powerful water-cooled mercury arc was surrounded by a concentric jacket containing the solution to be irradiated, a saturated solution of hydrazobenzene in alcohol. The solution, which is colourless at the start, becomes coloured as the reaction proceeds, owing to the formation of azobenzene. It is important to exclude air as completely as possible, as azobenzene is produced comparatively rapidly by aerial oxidation, a reaction doubtless accelerated by light; the preparation of the solution and the reaction itself were therefore carried out in an atmosphere of nitrogen freed from oxygen.

The concentration of the azobenzene, deduced from the colour of the solution, increases as the irradiation is prolonged, but appears to reach a limiting value after a few hours. A quantitative study of the reaction is practically impossible owing to two main factors: that the azobenzene absorbs strongly and probably acts as an inner filter, and that a number of side reactions also occur.

It was possible, however, to separate and identify aniline from the reaction. After irradiation the solution was steam distilled, bringing over aniline and some azobenzene which sublimes. After separating the azobenzene and extracting the aqueous solution with ether, and distilling off the ether, the aniline was obtained as an oily liquid. For further proof the acetyl derivative was prepared and the acetanilide identified by its melting-point and the mixed melting-point.

The photochemical primary process due to the continuous absorption in the near ultraviolet ${ }^{9}$ is most probably due to the primary process (8):

$$
\begin{equation*}
\underset{\mathrm{H}}{\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N}-\mathrm{NH}_{5} \mathrm{C}_{6}+h \nu=2 \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N} \cdot} \underset{\mathrm{H}}{ } . \tag{8}
\end{equation*}
$$

According to the above considerations the radicals would interact, giving aniline according to (9) *

followed by recombination (IO) yielding azobenzene :

$$
\begin{equation*}
2 \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N} \cdot \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N}=\mathrm{NC}_{6} \mathrm{H}_{5} \tag{10}
\end{equation*}
$$

Probably the result of the dimerisation is the trans-azobenzene with dipole moment zero. $\dagger$ The other alternative would give azobenzene and hydrogen according to ( 10 '):

$$
\begin{array}{c:ccc}
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N} \cdot & \mathrm{NC}_{6} \mathrm{H}_{5} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N}=\mathrm{NC}_{0} \mathrm{H}_{5}+\mathrm{H}, \quad \text { ( } \mathrm{o}^{\prime} \text { ) } \\
\hdashline \mathrm{H} & \mathrm{H}
\end{array}
$$

but this can be excluded as no hydrogen gas was found.

[^38]
## 3.

The mechanism of the interaction between OH radicals contains some controversial points and much work has been devoted to it in recent years. Rodebush and Wahl ${ }^{10}$ and Oldenberg ${ }^{11}$ have investigated the discharge reactions in water vapour, where the OH radicals are formed according to (II):

$$
\begin{equation*}
\mathrm{H}_{2} \mathrm{O}+\text { electron }=\mathrm{OH}+\mathrm{H}+\text { electron } . \tag{II}
\end{equation*}
$$

They found that a considerable amount of $\mathrm{H}_{2} \mathrm{O}_{2}$ was present in the pumped-off gases, which they attributed at first to the recombination

$$
2 \mathrm{OH}=\mathrm{H}_{2} \mathrm{O}_{2}
$$

in the gaseous state. In a later investigation Rodebush and Campbell ${ }^{12}$ showed that $\mathrm{H}_{2} \mathrm{O}_{2}$ was apparently not formed in the gaseous statebecause it could not be detected if the rapidly pumped-off gases werecooled in an ice trap (which was shown in itself to be capable of condensing $\mathrm{H}_{2} \mathrm{O}_{2}$ vapour). $\mathrm{H}_{2} \mathrm{O}_{2}$ could only be detected if a liquid air trapwas interposed and they concluded that $\mathrm{H}_{2} \mathrm{O}_{2}$ was apparently formed within the liquid air trap. They also found that no oxygen atoms and no appreciable amount of $\mathrm{O}_{2}$ were present in the discharge, which would not be in agreement with reaction (4).

Taking into account all the experimental facts, it can be shown that reaction (4) actually represents the interaction of OH radicals, and that the $\mathrm{H}_{2} \mathrm{O}_{2}$ formed is due not to the recombination of OH but to a mechanism similar to that assumed in the photochemical reaction. between $\mathrm{H}_{2}$ and $\mathrm{O}_{2}{ }^{6}$

We must remember that in the water vapour discharge we havefairly high concentrations of both OH and H . First of all the $\mathrm{OH}^{-}$ radicals react according to reaction (4), giving $O$ atoms by a very rapid reaction. Bonhoeffer and Pearson ${ }^{3}$ have shown that in this case it is not difficult to explain the absence of hydrogen peroxide. If, on the other hand, $\mathrm{H}_{2} \mathrm{O}_{2}$ is formed in appreciable quantities, the following. reactions have to be taken into account.

$$
\begin{equation*}
\mathrm{O}+\mathrm{OH}+(\mathrm{M})=\mathrm{HO}_{2}+(\mathrm{M})+55 \mathrm{k} . \mathrm{cal} \tag{12}
\end{equation*}
$$

and possibly also $\mathrm{O}+\mathrm{OH}=\mathrm{H}+\mathrm{O}_{2}+15 \mathrm{k} . \mathrm{cal}$.
and $\quad \mathrm{H}+\mathrm{O}_{2}+(\mathrm{M})=\mathrm{HO}_{2}+(\mathrm{M})$.
Reactions (I2) and (I3) can also proceed as heterogeneous processes, for instance on the walls of the vessel. The $\mathrm{HO}_{2}$ radicals formed from the above reactions can yield $\mathrm{H}_{2} \mathrm{O}_{2}$ and $\mathrm{O}_{2}$, according to reaction (7) which has been studied by Bates and Sally. ${ }^{6}$ On the above mechanism no appreciable amounts of $\mathrm{O}_{2}$ molecules should be present in the discharge. They will either disappear according to reaction (I3), or will give 0 atoms through the discharge according to (I4):

$$
\begin{equation*}
\mathrm{O}_{2}+\text { electron }=\mathrm{O}+\mathrm{O}+\text { electron } \tag{I4}
\end{equation*}
$$

as has been shown by Harteck and Kopsch. ${ }^{13}$
However, the stationary concentration of $O$ atoms present in thedischarge may be somewhat small, as was found by Rodebush and Wahl ${ }^{10}$ in the case of a weak discharge. This can be shown in the

[^39]following way. From the above equations, and taking into account the recombination of oxygen atoms according to :
\[

$$
\begin{equation*}
\mathrm{O}+\mathrm{O}+(\mathrm{M})=\mathrm{O}_{2}+(\mathrm{M}) \tag{15}
\end{equation*}
$$

\]

the stationary O -atom concentration $[\mathrm{O}]_{\mathrm{s}}$ is given by:
$\frac{\mathrm{d}[\mathrm{O}]_{\mathrm{s}}}{\mathrm{d} t}=k_{4}[\mathrm{OH}]^{2}-\left(k_{12}[M]+k_{12}\right)[\mathrm{OH}][\mathrm{O}]_{s}+k_{14}\left[\mathrm{O}_{2}\right]-k_{15}[\mathrm{O}]_{5}{ }^{2}[\mathrm{M}]=0$,
and

$$
\begin{align*}
{[\mathrm{O}]_{\mathrm{G}}=[\mathrm{OH}]\left\{\sqrt{\left(\frac{k_{12}[\mathrm{M}]+k_{12}}{2 k_{15}[\mathrm{M}]}\right)^{2}+\frac{k_{4}}{k_{15}[\mathrm{M}]}+\frac{k_{14}\left[\mathrm{O}_{2}\right]}{k_{15}[\mathrm{M}][\mathrm{OH}]^{2}}}\right.} \\
\left.-\frac{k_{12}[\mathrm{M}]+k_{12}}{2 k_{15}[\mathrm{M}]}\right\} \tag{16}
\end{align*}
$$

Reaction (4) is a very rapid reaction. It is also to be expected that reaction ( $12^{\prime}$ ) has a very small heat of activation, because the $O$ atom can approach the OH radical in the direction of its free valency without encountering repulsive forces.

Therefore, if $k_{12}^{\prime} \sim k_{4}$ and $\left(\frac{k_{12}[\mathrm{M}]+k_{12}^{\prime}}{2 k_{15}[\mathrm{M}]}\right)^{2}>\frac{k_{4}}{k_{15}[\mathrm{M}]}$ then :-
(i) reeak discharge : $\frac{k_{14}\left[\mathrm{O}_{2}\right]}{k_{15}[\mathrm{M}][\mathrm{OH}]^{2}} \ll\left(\frac{k_{12}[\mathrm{M}]+k_{12}{ }^{\prime}}{2 k_{15}[\mathrm{Mi}]}\right)^{2}$

$$
\left[\mathrm{O}_{\mathrm{s}} \sim \frac{k_{4}[\mathrm{OH}]^{2}+k_{14}\left[\mathrm{O}_{2}\right]}{\left(k_{12}[\mathrm{M}]+k_{12}\right)[\mathrm{OH}]}\right.
$$

which is very small.

$$
\text { (ii) strong discharge: }[\mathrm{O}]_{\mathrm{s}} \sim \sqrt{\frac{k_{14}\left[\mathrm{O}_{2}\right]}{k_{15}[\mathrm{M}]}} \text {. }
$$

The reason why hydrogen peroxide can be detected only with a liquid air trap but not with an ice trap is probably the following. It is quite possible that in the streaming system OH radicals or H or O atoms get into the trap. The interactions of these radicals or atoms will themselves have very low heats of activation, and will go on rapidly even at the temperature of liquid air. However, this is not the case for the interaction of these radicals and atoms with hydrogen peroxide as, for instance,

$$
\begin{gather*}
\mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{OH}=\mathrm{H}_{2} \mathrm{O}+\mathrm{HO}_{2}  \tag{16a}\\
\mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{H}=\mathrm{H}_{2} \mathrm{O}+\mathrm{OH}  \tag{16b}\\
\mathrm{H}_{2} \mathrm{O}_{2}+\mathrm{O}=\mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2} \tag{16c}
\end{gather*}
$$

All these have appreciable heats of activation, probably ${ }^{14,15} \sim 10 \mathrm{k.cal}$. Whereas reactions of the type ( $16 a$ ), ( $16 b$ ), ( $16 c$ ) are quite appreciably diminished at - $180^{\circ} \mathrm{C}$., they may cause a very rapid decomposition of hydrogen peroxide in an ice trap where the temperature is not lower than $0^{\circ} \mathrm{C}$.

## Summary.

1. Radicals show a different behaviour according as they possess a permanent dipole moment or not. In the latter case, recombination of the

[^40]radicals occurs very often. In the former case the electrostatic interaction of the molecular dipoles favours the dismutation. It practically always takes place if the activation energy of the dismutation reaction is sufficiently low, which is often the case if a hydrogen atom or electron has to be transferred to form two saturated reaction products.
2. The interaction of OH and $\mathrm{C}_{8} \mathrm{H}_{5} \mathrm{NH}$ radicals has been discussed in detail. The $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}$ radicals are formed by irradiation of an alcoholic solution of hydrazobenzene in the ultraviolet. The final products of this photochemical reaction are aniline and azobenzene, which are formed with a quantum efficiency appreciably smaller than unity.

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## A SURFACE INTERACTION BETWEEN FERRIC AND MAGNESIUM OXIDES.

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

Received 3Ist May, 1940.
In a previous paper ${ }^{1}$ it was shown that nickel oxide, when evaporated on to single crystals of corundum, crystallised in certain specific orientations with respect to the substrate crystal ; the presence of an interface compound of the spinel type was observed, and further heating of the specimen resulted in all the nickel oxide combining to form this compound, $\mathrm{NiO} . \mathrm{Al}_{2} \mathrm{O}_{3}$. In pursuance of the study of reactions of this type, a striking example has been found in the surface interaction of ferric oxide and magnesium oxide.

A piece of iron foil was completely oxidised by heating in air, and the resultant flake of oxide was placed parallel and close to the fresh cleavage surface (the cube face) of a crystal of periclase ( MgO ), and the two heated together for about ten minutes at approximately $900^{\circ} \mathrm{C}$. in an oxidising fiame. The surface of the periclase was found to be coloured pale yellow. Electron diffraction patterns were taken in the [roo] and [IIo] azimuths of the periclase at about 50 kv . with a 22 cm . camera length. The patterns of Figs. I and 2 respectively were obtained (Plate XI).

The spot patterns are similar to those obtained by electron diffraction from single crystals of ordinary spinel ( $\mathrm{MgO} . \mathrm{Al}_{3} \mathrm{O}_{3}$ ) in the corresponding azimuths. The Kikuchi line patterns are those of magnesium oxide. On the plate of Fig. I, taken in the [100] azimuth, there is a system of faint, sharp "irrational spots" (of the type observed first by Kirchner, Lassen and Bruck ${ }^{2}$ in silver films evaporated on to rocksalt) the most intense of which lie immediately outside the zero-order Laue zone at normal spots. The difference in the unit of pattern in the zero-order Laue zone from that in the other zones is due to the fact that the hko type spots for which $h+k=4 n+2$ are "forbidden." The pattern obtained in the [IIo] azimuth (Fig. 2) is also similar to that obtained from the corresponding azimuth of spinel, the presence of certain "forbidden" hko type diffractions being due to double scattering. In this pattern some irrational diffractions of the type mentioned above are present.
${ }^{1}$ H. R. Thirsk and E. J. Whitmore, Trans. Faraday Soc., 1940, 36, 565.
${ }^{2}$ H. Lassen, Physik. Z., 1934, 35, 172: H. Lassen and L. Bruck, Ann. Physik, 1935, 22, 65; F. Kirchner and H. Lassen, ibid., 24, 173.

The sharp spot pattern of the spinel type is evidently due to transmission of the electron beam through small crystals of the deposited film which have a spinel structure and are accurately orientated with respect to the substrate crystal. The presence of intense double diffraction supports this view of the structure of the deposit. Any continuous film on the surface must be very thin in view of the strength of the Kikuchi line pattern of the periclase substrate. The faint irrational diffractions show that there is some twinning on the octahedral planes of the deposited crystals. Of these diffractions, some in Fig. I would appear to require the presence of a hybrid close packed lattice similar to that discussed by Menzer ${ }^{3}$ and Goche and Wilman, ${ }^{4}$ but the absence in Fig. 2 of corresponding diffractions seems to indicate that the alternative explanation of their appearance (previously advanced by the authors, ${ }^{1}$ and by Wilman " for electron diffraction patterns taken from both metallic and non-metallic films), namely, that of double diffraction between the normal and twinned crystals is the correct one. The dimensions of the cubic unit cell of the deposit are exactly twice those of the magnesium oxide, i.e. $a_{0}=8.40 \mathrm{~A}$. The deposit would thus appear to consist of $\mathrm{MgO}, \mathrm{Fe}_{2} \mathrm{O}_{3}$.

## Summary.

The film formed by evaporation of ferric oxide on to a heated magnesium oxide crystal is found to consist of crystals of a substance of spinel structure apparently $\mathrm{MgO} . \mathrm{Fe}_{2} \mathrm{O}_{3}$, which are orientated parallel to the magnesium oxide lattice, and which yield diffractions indicating slight twinning on octahedral planes. The patterns show that intense double diffraction occurs.

Applied Physical Chemistry Laboratories, Imperial College of Science and Technology, London, S.W. 7.<br>${ }^{3}$ G. Menzer, Z. Krist., 1938, 99, 378.<br>${ }^{\circ}$ O. Goche and H. Wilman, Proc. Physic. Soc., 1939, 51, 625.<br>${ }^{6}$ H. Wilman, ibid., 1940, 52, 323.

## THE ELECTROLYTIC GROWTH OF IONIC CRYSTALS.

By A. R. Ubbelofide.

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The object of this paper is to draw attention to a curious phenomenon in the growth of crystals, which does not seem to have been previously described. Details are first given of an easy demonstration of the phenomenon. The experiments and discussion which follow aim at defining its scope, though current events have made it impossible to investigate all the implications.

## Demonstration.

The phenomenon of electrolytic growth can be very readily demonstrated for supersaturated solutions of $\mathrm{CuSO}_{4}$ in water. A convenient solution is obtained by dissolving about 100 g . of the pentahydrate in

150 g . water. Such a solution, when filtered hot with reasonable care to prevent the entry of dust into the receiver, can be kept in pyrex receivers about 12 hours at $20^{\circ} \mathrm{C}$. without depositing crystals spontaneously. The temperature can be controlled by circulating water outside the receiver.

If a pair of Cu electrodes are dipped into this solution, and a very small current is passed, crystals begin to deposit almost immediately, and practically all on the anode. A convenient source of pure Cu with a physically standardised surface is freshly uncovered D.C.C. copper wire. With 18 gauge wire and electrodes immersed 5 cm ., a current of 5 milliamp. gives a beautiful deposit of crystals on the anode within 10 minutes at $20^{\circ} \mathrm{C}$.

Experiments on the Electrolytic Growth of Crystals.-These experiments can be briefly summarised as follows :-
(I) The growth of crystals on the anode is not due to anodic etching providing a rough surface, since when the same pair of electrodes have their positive and negative signs reversed at intervals the crystals practically all deposit on the positive pole, irrespective of its previous history. Again, a blank wire added as a floating third electrode, insulated from the others, does not attract crystals, even if previously etched by making it an anode in a hot solution.

The inference from these experiments is that the deposition of crystals is connected with the actual passage of current.
(2) The material of the electrodes is important. A choice of electrode materials is limited by the fact that they must conduct a current, and must not deposit Cu on their surface by galvanic action with $\mathrm{CuSO}_{4}$. This excludes more electropositive metals such as Fe and Ni . On passing the same current through the supersaturated solution in a series of vessels under comparable conditions, but using electrodes of $\mathrm{Cu}, \mathrm{Pt}, \mathrm{C}$ and W , it was observed that electrolytic growth only took place easily on the copper anode.
(3) A survey of other salts which might show comparable growth on the appropriate electrodes is somewhat hampered by the spontaneous galvanic action which occurs with many metals even in solutions of their own salts.

Definite effects have been obtained in the case of $\mathrm{NiSO}_{4}$, which crystallises on a Ni anode, from supersaturated solutions, almost as easily as $\mathrm{CuSO}_{4}$ on a Cu anode. $\mathrm{MgSO}_{4}$ will crystallise on a Mg anode under conditions where no crystallisation takes place on a Pt anode. Basic copper acetate was observed to crystallise at a Ni anode. Negative results were obtained in most, but not all, attempts to crystallise $\mathrm{AgNO}_{3}$ on Ag electrodes, and lead acetate on Pb electrodes. In all cases where a preferential deposition was observed on one of the electrodes, this was the anode.
(4) The electrolytic growth of crystals can be a valuable means of studying the phenomena of supersaturation and crystal growth, owing to the ease with which certain factors can be controlled. The following experiments have been restricted to the system $\mathrm{Cu} / \mathrm{CuSO}_{4}$, and should not be regarded as more than first steps in a field where the control of experimental conditions has hitherto been difficult.

It is important to decide whether the electrolytic growth of crystals is mainly a transport phenomenon, or whether the processes occurring at the electrodes owing to the discharge of ions also control the growth. If transport is decisive, the number of distinct nuclei growing at an
electrode would depend mainly on the quantity of electricity passed through the supersaturated solution. If surface processes are important, the current density might be a controlling factor. Counts of the number of nuclei growing under various conditions should strictly be averaged over a large number of experiments, and the data which follow only indicate the order of magnitude of the effects observed.
(a) A number of experiments showed that when the surface of the electrodes is kept constant, and the quantity of electricity passed decreases, the number of nuclei growing also decreases.

In a typical experiment, the Cu electrodes were 0.16 cm . diameter, and immersed 5 cm . in the standard solution at $16^{\circ} \mathrm{C}$., and r .5 cm . apart. A current of $4.6 \mathrm{~m} . \mathrm{a}$. deposited about 100 nuclei in 15 minutes, and a current of $0.76 \mathrm{~m} . \mathrm{a}$. about 20 nuclei under comparable conditions. Preferential growth on the anode was observed even with currents as small as 0.2 m.a. Below this value, concentration differences in the $\mathrm{CuSO}_{4}$ solution, and strains in the Cu wire, give rise to local currents comparable with that measured, and lead to a bigger proportion of "stray " crystals growing on the cathode.
(b) Keeping the total quantity of electricity constant, the surface of the anode was increased, both by increasing the number of positive wires symmetrically placed round the cathode, and by using Cu foil in place of wire. This led to a small decrease in the total number of crystals growing. With a current density of $6 \cdot 10^{-4}$ amp. $/ \mathrm{cm} .^{2}$ the number of nuclei was not more than $30 \%$ larger than with a current density of $\mathrm{I} \cdot \mathrm{IO}^{-4} \mathrm{amp} . / \mathrm{cm} .^{2}$, i.e. the number of nuclei per unit surface decreases with decreasing current density. Copper foil did not give as many crystals as Cu wire of the same surface, though the purity of the metal in the foil was questionable.

Keeping the total quantity of electricity constant, and increasing the current density by using finer Cu wire for the electrodes, led to a decrease in the total number of crystals growing on the anode. The number per unit surface was, however, increased. In a typical experiment at $15^{\circ} \mathrm{C}$., a current density of $4 \times 10^{-4} \mathrm{amp} . / \mathrm{cm} .^{2}$ gave about 16 nuclei $/ \mathrm{cm} .^{2}$ in 15 minutes, and a current density of $36 \cdot 10^{-4} \mathrm{amp} . / \mathrm{cm} .{ }^{2}$ gave about 60 nuclei $/ \mathrm{cm} .^{2}$ during the same time.

From experiments of this kind it may be inferred that both the total transport and the current density are controlling factors in electrolytic growth.
(c) Amongst other results of interest, it was observed that with an alternating current ( 50 cycles $/ \mathrm{sec}$.) crystals were deposited on both electrodes. The crystals usually show indications of a preferential though not unique orientation with respect to the surface on which they grow. Furthermore, as the temperature of the supersaturated solution is raised, so as to decrease the degree of supersaturation, some decrease was observed in the number of crystals growing at the anode, at constant current and current density.

## Discussion.

No attempt will be made here to give a final interpretation of the phenomenon investigated in these experiments. It is, however, of some value to discuss its relation to other investigations on crystal growth.

The most direct comparison is with the formation of metal crystals, from a stream of vapour impinging on a foreign surface such as glass.

In the case of Cd , for example, it was found by Cockroft ${ }^{1}$ that the chance of crystals forming on a surface increased with increasing current density of atoms impinging on it. This was ascribed to the fact that co-operation between Cd atoms adsorbed on neighbouring sites on the glass facilitates the formation of a coherent deposit.

A typical calculation for the electrolytic growth of $\mathrm{CuSO}_{4}$ on the anode may be made as follows: A current density of $4 \cdot 10^{-4}$ amp. $/ \mathrm{cm} .^{2}$ corresponds with the impact of about $1 \cdot 26 . \mathrm{IO}^{15}\left(\mathrm{SO}_{4}\right)^{\prime \prime}$ ions per $\mathrm{cm} .^{2}$ per sec. Since about 16 crystals/cm. ${ }^{2}$ grow in 900 secs., the fraction of ionic impacts leading to nucleus formation is about $1.4 \times 10^{-17}$. With a current density nine times as large the number of nuclei per $\mathrm{cm} .^{2}$ rises to about 60 in 900 secs., but the fraction of effective impacts drops to about $6 \cdot \mathrm{IO}^{-18}$.

Taking the atomic volume of Cu as about $7 \cdot \mathrm{I}$ c.c./g. atom the number of Cu atoms $/ \mathrm{cm} .^{2}$ of surface is about $\mathrm{I} \cdot 9 \times 10^{15}$. If the surface of the anode is removed in a uniform manner by electrolysis, this means that when the current density is $4 \times 10^{-4} \mathrm{amp} . / \mathrm{cm} .^{2}$ corresponding sites in the surface suffer 0.66 impacts/second, and when the current density is $36 \times 10^{-4} \mathrm{amp} . / \mathrm{cm} .^{2}$ the number of impacts per site is about six per second.

From these figures it will be seen that the fraction of effective impacts, leading to nucleus formation, is very small. This is probably due to the smallness of the interval during which an $\left(\mathrm{SO}_{4}\right)$ ion remains adsorbed on the surface of the copper after discharge, so that co-operation between neighbours to form a crystal nucleus is infrequent. By making assumptions about the mechanism of discharge, more detailed calculations can be made about the probability of nucleus formation. These are not given here, owing to the desirability of using data averaged over a larger number of experiments.

Comparison should also be made between the phenomenon of electrolytic growth, and the formation and growth of crystal nuclei in melts and solutions. In a large number of melts and solutions, particularly of organic compounds, crystallisation will only begin on foreign particles with a suitable surfacc. ${ }^{2}$ Electrophoretic experiments have recently shown in a number of cases that these particles are electrically charged with respect to the solution or melt. ${ }^{3}$ The potential gradients in such experiments are much larger than in the phenomenon of electrolytic growth, and if the growth at the anode were due to the migration of colloids in the supersaturated solution it would be difficult to explain why no crystallisation takes place in the absence of a current, and why the material of the anode is important.

Ionic crystals are known, however, ${ }^{4}$ such as $\mathrm{CaF}_{2}$, for which formation and growth from supersaturated solutions appear to take place independently of the presence of foreign colloids. The cluster of ions corresponding with such crystals at a very early stage in their growth will usually be electrically charged with respect to the bulk of the solution. This charge arises partly from the fact that the free energy of a small particle can usually be lowered by the formation of an electrical double layer, and partly from the fact that there must usually

[^41]be a Nernst diffusion potential between the immediate surface of a growing crystal, and the bulk of the solution. ${ }^{5}$ The possibility cannot, as yet, be excluded that the phenomenon of electrolytic growth is due to the migration of such clusters towards the anode. As soon as a partial discharge takes place, the stability of the cluster with respect to the supersaturated solution would be upset, and growth might follow,

Whatever be the mechanism, the small currents at which electrolytic growth can be observed suggest that it may intervene in such phenomena as localised deposition of scale in boilers, and more especially in the innumerable biological examples of bones, teeth, and shells, where the crystals deposited from supersaturated solutions must have been directed in some way to their appropriate places in the organism.

## Summary.

Experiments are described to illustrate the phenomenon of electrolytic growth, in which supersaturated solutions of salts begin to deposit crystals at one of the electrodes when a small current is passed. In the discussion, reference is made to the mechanism of ionic discharge, to the migration of possible ionic clusters in solution, and to the biological importance of a mechanism for directing the deposition of crystals from supersaturated solutions.

The Davy Faraday Laboratory, The Royal Institution.<br>${ }^{5}$ Cf. perhaps A. Tschermak, Z. K'rist., 1931, 79, 465.

## REVIEWS OF BOOKS.

Introduction to Chemical Physics. By J. C. Slater. Pp. 52 I. McGraw Hill (1939). 33 s.

Chemistry is the science of atoms and of the way they combine. Physics deals with the interatomic forces and with the large-scale properties of matter resulting from these forces. Chemical Physics is the name used for the overlapping field in which both physicists and chemists should be trained. This book is an attempt to incorporate some of the material of this common field in a unified presentation. The effort has been made to produce a book which is intelligible without studying theoretical physics first.

In the matter of arrangement the author has departed from the logical order in the interest of easy presentation. Thermodynamics and statistical mechanics come first. Then gases, solids and liquids, including binary mixtures, are treated on the basis of thermodynamics with a minimum use of a model. Finally, atomic and molecular structure are introduced, together with a discussion of different types of substances, such as ionic crystals, homopolar compounds, organic molecules, silicates and metals.

The above remarks taken almost verbatim from the preface adequately describe the scope and object of the book, and I need discuss only the execution. As compared with any text-book of general physical chemistry,
this book is incomparably more accurate. The treatment is, however, so condensed as to make difficult reading. A typical example is the description of the spectroscopic $s, p, d$ notation on page 339 :-

Following spectroscopic notation, all the levels of a given 1 value are grouped together to form a series and are denoted by a letter. Thus $I=0$ is denoted by $s$ (for the spectroscopic Sharp series), $1=1$ by $p$ (for the Principle series), $l=2$ by $d$ (for the Diffuse series).
What could be more exact, precise and clear for the reader who already knows it, or more incomprehensible for the reader who does not? This unfortunate quality of unreadability could have been avoided either by restricting the ground covered or by increasing the length of the book.

References to experimental data are extremely scanty, and references to the literature completely absent. Only a list of text-books is given.

In comparison with the very high standard of accuracy in matters physical, I noticed some surprisingly elementary errors of chemistry and of mathematical terminology. For example-page 15I : the suggestion that the combination of hydrogen and oxygen is a simple termolecular reaction is misleading, and gives the erroneous impression that the equilibrium condition is determined by the reaction mechanism. Page 271: It is stated that a solution of sugar in water can exist only when a relatively small amount of sugar is mixed with a relatively large amount of water. This is untrue. Page 428 : There is confusion between an ester and a salt of an organic acid. Page 446: There is confusion between rhodium and rhenium. Page 448 : There is a reference to " the two valences of manganese "; in chemical terminology manganese can have five different valences, namely, two, three, four, six or seven. Page 70: " Product of terms." Mathematicians speak of sums of terms and products of factors. Page 298: The statement that the curve cannot be expressed analytically is untrue. Presumably what is meant is that $w$ cannot be expressed as an explicit function of $T$, although $T$ can be expressed as an explicit function of $w$. Page 409: "Of the order of magnitude of twotenths of I per cent." is verbose and meaningless. Why not " approximately 0.2 per cent. ?" The expression "of the order of" has a very special mathematical meaning, and should not be used here and at many other places to denote " approximately." Incidentally the prefix denoting thousand-fold is not Kilogram- but Kilo-.

The impression left on me by reading the book can perhaps be epitomised as follows. Suppose a student asked my advice whether he should read this book. If he were a very promising student, I should reply: "By all means try, but do not be discouraged if you find it too much for you." Suppose, on the other hand, he asked my advice as to the best method of becoming a proficient chemical physicist. I should unhesitatingly reply: "Go to M.I.T. and study under Professor Slater."
E. A. G.

Alternating Current Bridge Methods. By Dr. B. Hague. Pp. xvii +587 . (London: Sir Isaac Pitman \& Sons, Ltd., 1938. Price 25s. net.)
Dr. Hague's standard treatise is too well-known and appreciated to demand a detailed review. In this, the fourth edition, matter that appeared as an appendix to the third edition has been incorporated in the main
body of the text, and major developments in the subject to the end of 1937 have been included. Circuit locus diagrams are discussed, and a complete classification of bridges has been added.

The treatment is clear and comprehensive, and the book is quite indispensable to any serious student of a most important branch of applied physics.
A. F.

Thermodynamics and Chemistry. By F. H. Macdougall. (New York: John Wiley \& Sons, Inc. London: Chapman \& Hall, Ltd. Third edition, 1939. Pp. ix +491 . Price 30s. net.)

This, the third edition of a well-known textbook, has been produced in response to the request of the publishers to rewrite the book in accordance with modern thermodynamic practice, and it should be said at once that the author has carried out the task with signal thoroughness and success. It is largely a new book, and a very valuable one. Not much originality is attempted, but the exposition is extremely careful and thorough; and the author's skill and experience as a teacher is shown by the many occasions on which he foresees and explains many of the difficulties which present themselves to the inexperienced student.

The fundamentals of thermodynamics are established in rather over a hundred pages, together with the principal properties of gases; there follows a short chapter on fusion and evaporation ; then one on the essentials of the Phase Rule, and the principal properties of chemical potentials; osmotic pressure is treated here. An excellent and concise account of some of the principal applications of the Phase Rule follows. For the rest of the purely thermodynamic part of the book, chemical potentials are used extensively, and their simplicity in use is clearly brought before the reader. Electrochemical problems, including an outline of the theory of strong electrolytes, and of ionic equilibria, are well discussed, and there is a section on phase boundary potentials and electromotive force, using electrochemical potentials. The final seventy pages of the book deal concisely with the third law, and provide also a brief but useful introduction to statistical methods.

Naturally, the book is not light reading; no comprehensive work on chemical thermodynamics is likely to be that, and the reviewer cannot think of any important application of thermodynamics to Chemistry which does not receive its fair share of attention. In the earlier part of the book, the mathematical methods are clearly explained, so that any reader with an elementary knowledge of calculus and some application should be able to study the book; in the final chapters more facility in mathematical technique is assumed. The book is progressive in pace, as a textbook should be; and there are abundant and well-chosen examples for the student to work himself.

This is a textbook of outstanding merit, which should be available to every scrious student and teacher of thermodynamics in honours classes at universities; and its comprehensiveness will render it valuable also as a work of reference.
N. K. A.

Thermodynamics for Chemical Engineers. By H. C. Weber. (London : Chapman \& Hall, Ltd., 1939. Pp. vii +264 . Price 19s. 6d.)
This volume is not very lively reading and, in itself, will hardly succeed in interesting a student in the subject. As a companion to lectures, however, it is probably extremely useful.

The first five chapters are concerned with the First Law, the Phase Rule, heat capacity and heat of reaction. The next three chapters, which are amongst the most valuable, deal with $P-V-T$ relations, vapour pressure and latent heat. Here the author gives many excellent graphs and tables of use to the chemical engineer, including, for example, the constants for the Beattie-Bridgeman equation of some eighteen common gases, pressureenthalpy tables, etc. The application of free expansion and the JouleThomson coefficient in gas liquefaction are not dealt with.

In Chapters IX to XIV the author introduces the Second Law and deals with the problems of heat engines, refrigeration and fluid flow. The concluding chapters, some of which are rather sketchy, are concerned with the fugacity of gases, activity and chemical equilibrium, electrode processes and finally with the Third Law.

Apart from the very numerous graphs and tables, references to the original literature are also given in good number. A feature of the volume is the usual excellent practice in American textbooks of encouraging the student to master the subject by the working out of examples. These are of a type in which thermodynamic principles are applied to actual processes.

In style and notation the thermodynamics is similar to that of Lewis and Randall. No inaccuracies have been detected.
K. G. D.

A Text-Book of Heat. By Professor H. S. Allen and Mr. R. S. Maxwell. (London: Macmillan \& Co., 1939. Part I. Pp. viii + I to $527+$ xvi. Price ros. Part II. Pp. viii +528 to $846+$ xi. Price 1os. 6d.)

Of the two parts into which this text-book is divided, the first part is, in the main, descriptive and experimental, and is intended for the use of students of Intermediate grade, or for those preparing for University scholarship examinations. The second part is more advanced in character, devotes greater attention to theoretical matters, and is intended for use by students reading for a Pass degree.

The book should be judged as a whole. There is complete continuity in its design, and it may be said that an intelligent study of its contents will form an excellent preparation for specialised reading for Honours. The hand of the skilled teacher is apparent on every page; those points of theory over which the student is apt to flounder are carefully and clearly expounded, and a due balance is kept between geometrical and analytical methods. The subject is developed from the historical side-a particularly apposite method of approach in a science such as Heat-and the historical matter introduced is lively, relevant and thoroughly interesting. The book is a welcome addition to the literature of the subject.
A. $F$.


Fig. I.-Film formed by evaporating ferric oxide onto periclase cleavage face ; [100] azimuth.


Fig. 2.- $[$ IIO $]$ azimuth.

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    Vapour Pressure.- (e) $\mathrm{H}_{2} \mathrm{SO}_{4}$; ibid., p. 1394 ; (f) $\mathrm{H}_{2} \mathrm{SO}_{4}$; I.C.T., Vol. III, p. 303; (g) NaCl; ibid., p. 297.

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    * In practice it is seldom that stresses in constrained swelling reach the high values shown in Fig. 7, which may, therefore, be drawn on a much larger scale, and the $(p ; V)$ lines may be taken as straight.

[^21]:    * These are the beech blocks referred to in a previous paper ${ }^{*}$ where the swelling in a single direction was prevented by clamps applied to the dry block. It will be seen that the hydrostatic pressure is a maximum when the restraint is applied in the direction of maximum swelling, i.e. tangentially. A longitudinal restraint is quite ineffective in preventing swelling and no pressure results.
    $\dagger$ Small samples of spruce impregnated with synthetic resin which was polymerised without pressure. Here the restraint is applied by the resin in all directions and, therefore, larger pressures are set up. Too much reliance must not be placed on the accuracy of the calculated pressures because heat treatment alone will have slightly altered the isothermal from that of the natural spruce, though the deficiencies in moisture content, which are referred to heat treated control samples, will be of the same order. The last two entries (in $90 \%$ and $98 \%$ humidity) are of interest in indicating that the resin is beginning to fail in tension, but quite apart from the calculated stresses, the simple observation, that between $90 \%$ and $98 \%$ humidity, the moisture content deficiency has fallen, shows that the stress on the wood must also have decreased. This is in accordance with observations on resin impregnated woods, many of which show almost normal moisture content and swelling values when held in a saturated atmosphere, or soaked in water, for long periods. These observations also support the assumption that the resin has not decreased the natural hygroscopicity of the wood.
    $\ddagger$ These are two samples of a commercial product formed by compressing impregnated veneer sheets and polymerising the resin under pressure. The constitution of this material is not accurately known, but the results show that if the alternate veneer plies are laid with the grain at right angles, a lower equilibrium moisture content results than when all the grain is parallel. This may at once be interpreted as signifying a larger stress in the former case, which is no doubt due to the extra restraint imposed on the tangential expansion by the longitudinal fibres lying across the grain and transmitted from layer to layer by shear stresses in the intervening resin film.

[^22]:    * The above method has assumed that the wood water aggregate of sitka spruce could be treated as a perfect gel to which Porter's osmotic pressure equation could be applied. Actually, however, this will not be the case where, as in wood, some of the water is held by capillary forces, and is separated from the " true gel," which consists of wood substance and water held together by forces of molecular sorption. The capillary water, therefore, stands in the same relation to the "true gel" as does pure water to a solution when these are separated by a semi-permeable membranc. Using approximate values for the amounts of "capillary" and "molecular" water which make up the total moisture content $m$ at any vapour pressure, I have calculated that, very close to saturation, the values of $\beta$ given above will be about $15 \%$ too low, and that the error decreases rapidly with vapour pressure until at $60 \%$ humidity, where there is no "capillary" moisture, $\beta$ will be correct. These differences are hardly signiflcant in view of the uncertainties of the data in the results given above.

    It is important to note that $\beta$ here applies only to constant "molecular" moisture content. An external pressure applied to wood will not be exerted on the "capillary" moisture because the lowered vapour pressure of this moisture exists only in virtue of its open curved meniscus. Thus while the vapour pressure of the "true gel" rises under external pressure, that of the "capillary" moisture will not, and some exchange of moisture between the two types of sorption must take place.

    The equilibrium of "capillary" and "molccular" moisture in a porous gel under stress is now being studied, and if useful conclusions can be drawn, I propose to make this the subject of a future paper, but in the meantime it seems important to draw attention to the infuence of capillary water in determining the properties of gels.

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    $$
    \mathrm{C}_{8} \mathrm{H}_{8} \mathrm{~N} \cdot+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}=\mathrm{C}_{8} \mathrm{H}_{5} \mathrm{NH}_{2}+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{O} .
    $$

    is appreciably endothermic.
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