No. 235.

# Transactions of the Faraday Society.

FOUNDED 1903.

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

Vol. XXXVI. Part 11. NOVEMBER, 1940. 5s.

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# THE RELATION BETWEEN POTENTIAL ENERGY AND INTERATOMIC DISTANCE IN SOME DIATOMIC MOLECULES.

By J. W. Linnett.

*Received 14th May and as amended on 1st August, 1940.*

The relation between the potential energy and the distance separating two bonded atoms is of the greatest importance in all chemical processes. It is the purpose of this paper to consider the functions that have been proposed to represent this relation. The best known of these was suggested by Morse,[1] but others have been formulated by Huggins [2] and by Sutherland.[3] The function to be used should provide an explanation of the relation that has been observed to exist between the interatomic distance and the force constant of the linkages formed by a given pair of atoms. This relationship has been put into several forms, the most commonly used being those due to Badger,[4] to Douglas Clark,[5] and to Fox and Martin.[6] The potential energy functions provide other relationships that can be tested between the four quantities, capable of experimental determination, which fix the position and shape of the curve obtained by plotting the potential energy against the interatomic distance. These are: (*a*) the equilibrium interatomic distance, (*b*) the fundamental vibration frequency or the force constant, (*c*) $\omega_e x_e$, which measures the departure from harmonicity in the neighbourhood of the minimum of the curve, and (*d*) the energy of dissociation.

In the following sections three types of potential function will be considered. These are:

(1) The double-reciprocal function:

$$V = \frac{a}{r^m} - \frac{b}{r^n}.$$

(2) The double-exponential function:

$$V = a \,.\, e^{-mr} - b \,.\, e^{-nr}.$$

(3) The reciprocal-exponential function:

$$V = \frac{a}{r^m} - b \,.\, e^{-nr}.$$

All these functions are made up of two terms, both of which are zero at $r = \infty$. The first term, which represents the repulsion between the

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[1] Morse, *Physic. Rev.*, 1929, **34**, 57.
[2] Huggins, *J. Chem. Physics*, 1935, **3**, 473; 1936, **4**, 308.
[3] Sutherland, *Proc. Ind. Acad. Sci.*, 1938, **8**, 341.
[4] Badger, *J. Chem. Physics*, 1934, **2**, 128; 1935, **3**, 710.
[5] Douglas Clark, *Phil. Mag.*, 1934, **18**, 459.
[6] Fox and Martin, *J. Chem. Soc.*, 1939, 884.

atoms, becomes large as $r$ approaches zero, while the second term, which represents the attraction between the atoms, becomes large in a negative sense as $r$ approaches zero. The behaviour of the whole expression depends on the relative values of the constants. The application of the third expression to diatomic molecules involving atoms of the first Period will be considered in detail.

### (1). The Double-Reciprocal Function.

By differentiating the function

$$V = \frac{a}{r^m} - \frac{b}{r^n} \tag{1}$$

and putting $\left(\frac{\mathrm{d}V}{\mathrm{d}r}\right)_{r=r_e} = 0$ and $\left(\frac{\mathrm{d}^2V}{\mathrm{d}r^2}\right)_{r=r_e} = k.$

Sutherland has shown that the following relationships are obtained

$$D = \frac{a}{r_e{}^m}\left(\frac{m-n}{n}\right) = \frac{b}{r_e{}^n}\left(\frac{m-n}{m}\right) \tag{2}$$

and

$$k = \frac{a\,.\,m}{r_e{}^{m+2}}(m-n) = \frac{b\,.\,n}{r_e{}^{n+2}}(m-n) \tag{3}$$

From these two equations we obtain

$$\frac{kr_e{}^2}{D} = mn \tag{4}$$

Elimination of $n$ and $b$ from the above expressions gives

$$\frac{kr_e{}^2}{D} = \frac{m^2}{1 + \frac{Dr_e{}^m}{a}} \tag{5a}$$

and

$$k\,.\,r_e{}^{m+2} = \frac{m^2\,.\,Dr_e{}^m}{1 + \frac{Dr_e{}^m}{a}} \tag{6a}$$

Or elimination of $m$ and $a$ gives

$$\frac{kr_e{}^2}{D} = \frac{n^2}{1 - \frac{Dr_e{}^n}{b}} \tag{5b}$$

and

$$kr_e{}^{n+2} = \frac{n^2\,.\,Dr_e{}^n}{1 - \frac{Dr_e{}^n}{b}} \tag{6b}$$

In the above equations $V$ and $D$ represent the potential energy and the energy of dissociation, and $r_e$ represents the equilibrium value of $r$, the separation of the two atoms.

The expression (6$b$) will explain the relationship $k\,.\,r_e{}^6 =$ a constant if $n$, $b$ and $D\,.\,r_e{}^n$ are constant and $n = 4$. This is equivalent to assuming that the attraction between the atoms remains constant for all electronic conditions. This certainly cannot be possible, since changes in the quantities $k$, $D$ and $r_e$ for different electronic states must be due in a large degree to changes in the attractive force between the atoms for the different states. On the other hand, $k\,.\,r_e{}^6 =$ a constant can also be explained on the basis of the expression (6*a*) if $m$, $a$ and $D\,.\,r_e^m$ are constant for all the electronic states, $m$ being equal to four. This is much more acceptable, since it is not unreasonable to suppose that the repulsion between the two atoms does not change greatly for different electronic states. However, if $m = 4$, equation (5*a*) indicates that $k\,.\,r_e^2/D$ must be less than $m^2$, that is less than 16. In most cases, however, $kr_e^2/D$ is greater than 16, so that this assumption is not justifiable. On any other explanation, the approximate constancy of $k\,.\,r_e^6$ must be due to changes in $a$ and $D\,.\,r_e^4$ being such as to maintain $\dfrac{16\,.\,Dr_e^4}{1 + \dfrac{Dr_e^4}{a}}$ equal to a constant and cannot be said to follow from the above form of the function. This simple function cannot therefore be regarded as being particularly satisfactory or helpful.

Recently Sutherland [7] has modified the double-reciprocal function by replacing $r$ by $(r - d)$, so that it becomes

$$V = \frac{a}{(r-d)^m} - \frac{b}{(r-d)^n} \quad . \quad . \quad . \quad (1a)$$

This function (1*a*) involves five adjustable constants instead of four which makes it less satisfactory on the grounds of simplicity than (1). The reasons for adopting (1*a*) are that plots of $(k/D)^{1/3}$ against $r_e$ are claimed to be linear for series of similar diatomic molecules. However, the scarcity of points on the graphs makes this rather unconvincing. In all cases there are three points close together and one much farther off, and it would be possible to draw almost any curve through the points. On examination of the three states of the oxygen molecule which have been investigated it is found that: (1) $^3\Sigma_u^-$ : $\left(\frac{k}{D}\right)^{\frac{1}{3}} = 3{\cdot}95$, $r_e = 1{\cdot}599$; (2) $^1\Sigma_g^+$ : $\left(\frac{k}{D}\right)^{\frac{1}{3}} = 4{\cdot}16$, $r_e = 1{\cdot}223$; (3) $^3\Sigma_g^-$ : $\left(\frac{k}{D}\right)^{\frac{1}{3}} = 3{\cdot}80$, $r_e = 1{\cdot}204$ A. There is no evidence here of $(k/D)^{\frac{1}{3}}$ varying linearly with $r_e$. Equally little evidence for the above linearity is shown by four states of $N_2$, by three states of $Li_2$, and by many other molecules. If $m$ and $n$ remain constant for the ground states of different molecules it would surely be expected that they would remain the same for different states of the same molecule.

Sutherland states that the most satisfactory values for $m$ and $n$ are 4 and 1, and for $d$ the value given by Badger. The explanation of the Badger relation is therefore

$$k(r_e - d)^{n+2} = \frac{n^2\,.\,D(r_e - d)^n}{1 - \dfrac{D(r_e - d)^n}{b}}$$

with $n = 1$. This expression involves either that (1) $D\,.\,(r_e - d)$ and $b$ both remain constant, or that (2) $D\,.\,(r_e - d)$ and $b$ both alter in such a way that the expression on the right-hand side of the above equation remains constant. The first explanation is unsatisfactory, since it involves the assumption that the attraction term is the same in all cases and all changes in $D$, $k$ and $r_e$ are due to changes in the repulsion term. The second is unsatisfactory, since it means that the constancy is purely fortuitous.

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[7] Sutherland, *J. Chem. Physics*, 1940, 8, 161.

### (2). The Double-Exponential Function.

In its most general form this function is :

$$V = a \, . \, \mathrm{e}^{-mr} - b \, . \, \mathrm{e}^{-nr}.$$

The Morse function is a special form of the above, in which

$$a = D \, . \, \mathrm{e}^{mr_e}, \quad b = 2D \, . \, \mathrm{e}^{nr_e}, \quad \text{and} \quad m = 2n.$$

In this equation there are only three independent constants. Since there are four measurable quantities, the magnitude of which is determined by the potential energy function, the equation must provide one relation between these quantities. This relation is $\mu \, . \, \omega_e x_e = C\left(\frac{k}{D}\right)$, where $\mu$ is the reduced mass of the diatomic molecule and $C$ is a constant which is the same for all molecules. As has been pointed out by Huggins, this relationship is but poorly obeyed in practice. Its failure will be dealt with more fully in a subsequent section.

The constants of the Morse function are chosen independently for each electronic state to fit the data. No relationship between the constants for the different electronic states of the same molecule has been suggested, so that the function offers no explanation of the relation between the force constant and the equilibrium interatomic distance.

Huggins has modified the Morse function by putting $a$ in equation (7) equal to $\mathrm{e}^{mr_{12}}$, both $r_{12}$ and $m$ being the same for all electronic states of the same molecule. The fixing of two of the constants enables Huggins to obtain from the observed values of $k$ and $\omega_e x_e$, calculated values of the equilibrium interatomic distances. The results obtained are encouraging, the average deviation from the observed distance being of the order of 2 %. However, when Huggins attempted to use the same function with the same values of $r_{12}$ and $m$ for calculating the heats of dissociation the results obtained were quite unsatisfactory. The discrepancies between the calculated and observed values of $D$ were in many instances of the order of 100 or 200 % of the observed value. It appears, therefore, that the function of Huggins, like that of Morse, gives an adequate representation of the relation between $V$ and $r$ in the neighbourhood of $r_e$, but departs widely from the actual relation outside this region. That is, satisfactory interconnection between $k$, $\omega_e x_e$ and $r_e$ is obtained, but values of $D$ calculated from them by application of the function are widely in error.

### (3) The Reciprocal-Exponential Function.

The general form of this function is :

$$V = \frac{a}{r^m} - b \, . \, \mathrm{e}^{-nr} \quad . \quad . \quad . \quad . \quad (8)$$

Differentiating it and putting $\left(\frac{\mathrm{d}V}{\mathrm{d}r}\right)_{r=r_e} = 0$ and $\left(\frac{\mathrm{d}^2V}{\mathrm{d}r^2}\right)_{r=r_e} = k$ provides the following relationships :

$$D = \frac{a}{r_e^{\,m}}\left(\frac{m - nr_e}{nr_e}\right) \quad . \quad . \quad . \quad . \quad (9)$$

and

$$k = \frac{a}{r_e^{\,m+2}} \, . \, m(m + 1 - nr_e) \quad . \quad . \quad . \quad (10)$$

Combination of (9) and (10) gives :

$$\frac{kr_e^2}{D} = m \, . \, nr_e\left(1 + \frac{1}{m - nr_e}\right) \quad . \quad . \quad . \quad (11)$$

Elimination of $nr_e$ from (10) and (11), using (9), leads to

$$\frac{kr_e^2}{D} = \frac{m^2}{1 + \dfrac{Dr_e^m}{a}} + \frac{ma}{Dr_e^m} \quad . \quad . \quad . \quad (12)$$

and

$$kr_e^{m+2} = ma + \frac{m^2 \, . \, Dr_e^m}{1 + \dfrac{Dr_e^m}{a}} \quad . \quad . \quad . \quad (13)$$

In the first place it is necessary to enquire to what extent this function explains the relationship between $k$ and $r_e$. If $m$ is equal to 4 and $a$ is a constant, $k \, . \, r_e^6$ is approximately constant provided that the second term on the right-hand side of equation (13) is not large compared with $ma$ and that it does not vary greatly. If $m$ is equal to 3 we have the Fox and Martin modification that $k \, . \, r_e^5$ is approximately constant. Detailed investigation which is discussed more fully later shows that the best results are obtained if $m$ has the value 3 for the molecules considered in this paper. With this value of $m$ and $a$ chosen separately for each molecule it is found that the first term on the right-hand side of equation (13) is always greater than half the total magnitude of the right-hand side of the equation. Also Fox and Martin [6] have pointed out that for the C—C links in the series ethane, ethylene and acetylene the value of $D \, . \, r_e^3$ remains approximately constant. In addition, the value of $\dfrac{9 \, . \, Dr_e^3}{1 + \dfrac{Dr_e^3}{a}}$ varies more slowly than $D \, . \, r_e^3$, since this quantity occurs both in the numerator and in the denominator. It is not unreasonable to assert, therefore, that the reciprocal-exponential function provides an explanation of the relation between $k$ and $r_e$.

One difficulty of the double-reciprocal function was its inability to explain the observed values of $kr_e^2/D$. No such difficulty exists in this case. For the whole function to have the correct form, it is necessary for $nr_e$ to be less than $m$. According to equation (11) the closer $nr_e$ approaches to $m$ the larger does $kr_e^2/D$ become, and since there is no limit to the closeness with which $nr_e$ approaches $m$ there is no upper limit to $kr_e^2/D$.

In order to explain the approximate relation between $k$ and $r_e$ it has been necessary to assume that $m$ and $a$ are constant for all states of a given molecule. This is equivalent to making the reasonable assumption, as Huggins did, that the repulsion term remains constant for all states.

To test the suggested reciprocal-exponential function various detailed calculations have been carried out. At the present time these are confined to molecules consisting of two atoms, both of which are members of the first period, *i.e.* Li to F. It is hoped to extend the function later to other molecules. Since for any given molecule only $m$ and $a$ are fixed, for each state of the molecule two quantities, namely $n$ and $b$, can be chosen to fit the facts. This means that in order to calculate any observable quantity it is necessary to obtain the values of $n$ and $b$

from two other observable quantities. The first test has been carried out by calculating $r_e$ from observed values of $k$ and $D$. For this equation (13) has been used. For all molecules $m$ has been taken to be 3 and $a$ has been given a value, different for each molecule, which gives the best reproduction of the observed facts. The second test that has been carried out is the calculation of $\omega_e x_e$ from $k$ and $D$. Lastly, $\omega_e x_e$ and $D$ have been calculated from observed values of $k$ and $r_e$. In the second and third tests the values of $a$ employed are those that were found to be most satisfactory in the first test.*

## (*a*) Calculation of $r_e$ from $k$ and $D$.

The results of this test are summarised in Table I. These results are compared with those obtained, using $k \, . \, r_e^6 =$ a constant, the constant for this expression being chosen separately for each molecule. For each molecule the final figure in the eighth column gives the mean percentage error in $r_e$ (calc.). The last figure in the eleventh column for each molecule gives the mean percentage error in $r_e$, calculated, using $k \, . \, r_e^6 =$ a constant, for that molecule. The figures calculated, using $k \, . \, r_e^5 =$ a constant, are, on the whole, not as good as those obtained using the sixth power of the interatomic distance. They have, therefore, been omitted from Table I. The values of $D$ given for the different states of BeO have been estimated on the basis of calculations of $D$, using the Morse function. Since this is an unsatisfactory method of obtaining $D$, the figures for BeO have been omitted from the present series of calculations.

The mean percentage error averaged over all the states considered in Table I is 1·5. The mean percentage error for the results, using the expression $k \, . \, r_e^6 =$ a constant, is 0·9, and for the results obtained, using $k \, . \, r_e^5 =$ a constant, 1·4. The above results show, therefore, that for the calculation of interatomic distances the $k \, . \, r_e^6$ relationship is to be preferred for, besides giving better results, it requires less initial data. If, however, the results in Table I are regarded merely as a test of the potential function, they must be regarded as being satisfactory. The agreement is closer than that obtained by Huggins over the same series of molecules, the mean percentage error obtained by him being about 2·0, though it must be remembered that he used fewer adjustable constants.

## (*b*) Calculation of $\mu \, . \, \omega_e x_e$ from $k$ and $D$.

Kratzer [8] has shown that for the potential energy function

$$V = E_s + c_2(r - r_e)^2 + c_3(r - r_e)^3 + c_4(r - r_e)^4,$$

the value of $\omega_e x_e$ is given by

$$\mu \, . \, \omega_e x_e = \left[\frac{15}{8}\left(\frac{c_3}{c_2}\right)^2 - \frac{3}{2}\left(\frac{c_4}{c_2}\right)\right]\frac{h}{8\pi^2 \, . \, c}$$

where $\mu$ is the reduced mass of the molecule.

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* In all the calculations the distances, force constants and dissociation energies were expressed in quantities based on a system in which the fundamental units were the Ångstrom, the gram and the second. The unit of force in this system is called the A. dyne ($= 10^{-8}$ dynes) and the unit of energy the A. erg ($= 10^{-16}$ ergs). The force constants are measured in A. dynes/A. which is numerically equal to dynes/cm. Dissociation energies are given in A. ergs per molecule (1 A. erg per molecule = 1·44 cal. per g. molecule = 6·24 × $10^{-5}$ electron volts). The data on the molecules considered are taken from Jevons' *Report on the Band Spectra of Diatomic Molecules*, Sponer's *Molekulspectren*, and Herzberg's *Molecular Spectra and Molecular Structure.*

[8] Kratzer, *Z. Physik*, 1920, 3, 289; see also Jevons, *Report on the Band Spectra of Diatomic Molecules*, p. 27.

TABLE I.—CALCULATION OF $r_e$ FROM OBSERVED VALUES OF $k$ AND $D$.

| Mol. | Observed. | | $r_e$. | $a$ $\times 10^{-5}$. | $r_e$ calc. from Eq. 13. | $r_e$ (calc.) $-r_e$ (obs.) | % Error. | $k \cdot r_e^6$ $\times 10^{-5}$. | Calc. $r_e$. | % Error. |
|---|---|---|---|---|---|---|---|---|---|---|
| | $k$ $\times 10^{-5}$. | $D$ $\times 10^{-4}$. | | | | | | | | |
| $Li_2$ . | 0·150 | 0·73 | 2·93 | 5·6 | 2·856 | −0·074 | −2·5 | 102 | 2·965 | +1·2 |
| | 0·131 | 1·99 | 3·11 | | 3·196 | +0·086 | +2·8 | | 3·033 | −2·5 |
| | 0·253 | 1·82 | 2·67 | | 2·703 | +0·033 | +1·2 | | 2·718 | +1·8 |
| | | | | | | | 2·2 | | | 1·8 |
| $C_2$ . | 11·30 | 4·94 | 1·261 | 8·4 | 1·238 | −0·023 | −1·9 | 46·6 | 1·266 | +0·4 |
| | 9·10 | 5·41 | 1·315 | | 1·307 | −0·008 | −0·6 | | 1·313 | −0·2 |
| | 9·48 | 8·76 | 1·308 | | 1·335 | +0·027 | +2·1 | | 1·304 | −0·3 |
| | | | | | | | 1·5 | | | 0·3 |
| $N_2$ . | 17·19 | 3·65 | 1·144 | 7·6 | 1·093 | −0·051 | −4·5 | 39·0 | 1·146 | +0·2 |
| | 12·32 | 7·60 | 1·207 | | 1·220 | +0·013 | +1·1 | | 1·212 | +0·4 |
| | 8·75 | 5·67 | 1·290 | | 1·299 | +0·009 | +0·7 | | 1·283 | −0·6 |
| | 22·82 | 11·70 | 1·094 | | 1·083 | −0·011 | −1·0 | | 1·093 | −0·1 |
| | | | | | | | 1·8 | | | 0·3 |
| $O_2$ . | 2·36 | 1·51 | 1·599 | 6·4 | 1·593 | −0·006 | −0·4 | 35·9 | 1·574 | −1·6 |
| | 9·63 | 5·55 | 1·223 | | 1·231 | +0·008 | +0·7 | | 1·245 | +1·8 |
| | 11·75 | 8·11 | 1·204 | | 1·204 | 0·000 | 0·0 | | 1·205 | +0·1 |
| | | | | | | | 0·4 | | | 1·2 |
| BeF | 4·92 | 3·03 | 1·390 | 4·8 | 1·322 | −0·068 | −4·9 | 35·7 | 1·391 | +0·1 |
| | 5·73 | 9·56 | 1·357 | | 1·386 | +0·029 | +2·1 | | 1·357 | 0·0 |
| | | | | | | | 3·5 | | | 0·1 |
| BO . | 6·26 | 5·19 | 1·301 | 5·5 | 1·323 | +0·022 | +1·7 | 28·1 | 1·337 | +2·7 |
| | 6·06 | 5·89 | 1·348 | | 1·346 | −0·002 | −0·1 | | 1·344 | −0·3 |
| | 13·59 | 10·51 | 1·199 | | 1·153 | −0·046 | −3·8 | | 1·175 | −2·0 |
| | | | | | | | 1·9 | | | 1·7 |
| CN . | 17·74 | 10·03 | 1·148 | 7·5 | 1·136 | −0·012 | −1·0 | 41·7 | 1·153 | +0·4 |
| | 12·11 | 9·14 | 1·236 | | 1·238 | +0·002 | +0·2 | | 1·229 | −0·6 |
| | 16·21 | 11·29 | 1·169 | | 1·170 | +0·001 | +0·1 | | 1·170 | +0·1 |
| | | | | | | | 0·4 | | | 0·4 |
| CO . | 9·26 | 3·19 | 1·232 | 7·0 | 1·228 | −0·004 | −0·3 | 37·0 | 1·260 | +2·3 |
| | 12·17 | 6·37 | 1·205 | | 1·193 | −0·012 | −1·0 | | 1·204 | −0·1 |
| | 18·90 | 15·9 | 1·128 | | 1·144 | +0·016 | +1·4 | | 1·119 | −0·8 |
| | | | | | | | 0·9 | | | 1·1 |
| NO . | 24·12 | 15·1 | 1·07 | 6·6 | 1·062 | −0·008 | −0·7 | 36·2 | 1·070 | 0·0 |
| | 4·72 | 4·60 | 1·413 | | 1·449 | +0·036 | +2·6 | | 1·405 | −0·4 |
| | 24·70 | 15·9 | 1·060 | | 1·060 | 0·000 | 0·0 | | 1·066 | +0·6 |
| | 15·91 | 9·71 | 1·146 | | 1·138 | −0·008 | −0·7 | | 1·147 | +0·1 |
| | | | | | | | 1·0 | | | 0·3 |
| $N_2^+$ | 23·95 | 5·10 | 1·071 | 8·6 | 1·051 | −0·020 | −1·9 | 37·0 | 1·075 | +0·4 |
| | 19·97 | 10·03 | 1·113 | | 1·131 | +0·018 | +1·7 | | 1·108 | −0·4 |
| | | | | | | | 1·8 | | | 0·4 |

TABLE I.—*Continued.*

| Mol. | Observed. $k$ $\times 10^{-5}$. | Observed. $D$ $\times 10^{-4}$. | $r_e$. | $a$ $\times 10^{-5}$. | $r_e$ calc. from Eq. 13. | $r_e$ (calc.) $-r_e$ (obs.) | % Error. | $k \cdot r_e^6$ $\times 10^{-5}$. | Calc. $r_e$. | % Error. |
|---|---|---|---|---|---|---|---|---|---|---|
| $O_2^+$ | 3·79 | 2·23 | 1·41 | 6·1 | 1·443 | +0·033 | +2·3 | 32·8 | 1·433 | +1·5 |
| | 16·51 | 10·2 | 1·14 | | 1·117 | −0·023 | −2·0 | | 1·121 | −1·7 |
| | | | | | | | 2·2 | | | 1·6 |
| $CO^+$ | 11·93 | 4·27 | 1·168 | 6·6 | 1·162 | −0·006 | −0·5 | 33·0 | 1·185 | +1·4 |
| | 9·84 | 7·30 | 1·212 | | 1·253 | +0·041 | +3·4 | | 1·223 | +0·9 |
| | 19·68 | 11·3 | 1·114 | | 1·093 | −0·021 | −1·9 | | 1·090 | −2·2 |
| | | | | | | | 1·9 | | | 1·5 |

The reciprocal-exponential function can be expanded as a power series in $(r - r_e)$, and in the neighbourhood of $r_e$ the higher terms in this series may be neglected. Using the above expression of Kratzer a value for $\omega_e x_e$ in terms of $m$, $n$ and $r_e$ can be obtained. This expression is

$$\mu r_e^2 \cdot \omega_e x_c = \frac{h}{64\pi^2 c}\left\{\frac{5}{3}\left[\frac{(m+1)(m+2)-(nr_e)^2}{(m+1)-nr_e}\right]^2 - \left[\frac{(m+1)(m+2)(m+3)-(nr_e)^3}{(m+1)-nr_e}\right]\right\}.$$

If $\mu$ is expressed in atomic weight units and $r_e$ in Ångstroms, this becomes, with $m = 3$:

$$\mu r_e^2 \cdot \omega_e x_e = 2{\cdot}098\left\{\frac{5}{3}\left[\frac{20-(nr_e)^2}{4-nr_e}\right]^2 - \left[\frac{120-(nr_e)^3}{4-nr_e}\right]\right\}.$$

The results obtained in the calculation of $\mu \cdot \omega_e x_e$ from $k$ and $D$ (and the values of $r_e$ calculated in test (*a*) and given in Table I) are summarised in Table II. The eighth column gives $\mu \cdot \omega_e x_e$, as calculated from the Morse potential energy function, which gives $\mu \cdot \omega_e x_e = 8{\cdot}39\ k/D$, and the ninth the error in this as a percentage. The final figures for each molecule in the seventh and ninth columns give the mean percentage errors for that molecule.

TABLE II.—CALCULATION OF $\mu\omega_e x_e$ FROM OBSERVED VALUES OF $k$ AND $D$.

| Mol. | $k$ (obs.) $\times 10^{-5}$. | $r_e$ (calc.) from Table I. | $n$ (calc.). | $\mu \cdot \omega_e x_e$ (calc.). | $\mu\ \omega_e x_e$ (obs.). | % Error. | $\mu \cdot \omega_e x_e$ (Morse). | % Error. |
|---|---|---|---|---|---|---|---|---|
| $Li_2$ . | 0·150 | 2·856 | 0·798 | 15·6 | 21·94 | − 29 | 17·3 | − 21 |
| | 0·131 | 3·196 | 0·435 | 7·18 | 5·25 | + 37 | 5·5 | + 5 |
| | 0·253 | 2·703 | 0·718 | 14·04 | 18·13 | − 23 | 11·7 | − 35 |
| | | | | | | 30 | | 20 |
| $C_2$ . | 11·30 | 1·238 | 2·18 | 112·4 | 116·1 | − 3 | 191·8 | + 65 |
| | 9·10 | 1·307 | 2·01 | 94·4 | 72·6 | + 30 | 141·0 | + 94 |
| | 9·48 | 1·335 | 1·80 | 77·2 | 70·0 | + 10 | 90·7 | + 30 |
| | | | | | | 14 | | 63 |

TABLE II.—*Continued.*

| Mol. | $k$ (obs.) × 10⁻⁵. | $r_e$ (calc.) from Table I. | $n$ (calc.). | $\mu . \omega_e x_e$ (calc.). | $\mu . \omega_e x_e$ (obs.). | % Error. | $\mu . \omega_e x_e$ (Morse). | % Error. |
|---|---|---|---|---|---|---|---|---|
| $N_2$ . | 17·19 | 1·093 | 2·58 | 159·9 | 184·8 | − 13 | 394·5 | + 114 |
| | 12·32 | 1·220 | 2·08 | 102·3 | 101·1 | + 1 | 135·8 | + 35 |
| | 8·75 | 1·299 | 1·99 | 93·2 | 97·5 | − 4 | 129·3 | + 33 |
| | 22·82 | 1·083 | 2·32 | 127·1 | 101·1 | + 26 | 163·4 | + 62 |
| | | | | | | 11 | | 61 |
| $O_2$ . | 2·36 | 1·593 | 1·72 | 70·2 | 85·7 | − 18 | 130·9 | + 53 |
| | 9·63 | 1·231 | 2·10 | 103·9 | 111·4 | − 7 | 145·3 | + 31 |
| | 11·75 | 1·204 | 2·04 | 99·1 | 95·9 | + 3 | 176·0 | + 83 |
| | | | | | | 9 | | 56 |
| BeF | 4·92 | 1·322 | 1·98 | 92·9 | 53·6 | + 73 | 136·0 | + 154 |
| | 5·73 | 1·386 | 1·41 | 54·1 | 55·7 | − 3 | 50·2 | − 10 |
| | | | | | | 38 | | 82 |
| BO . | 6·26 | 1·323 | 1·85 | 81·5 | 65·7 | + 24 | 101·0 | + 54 |
| | 6·06 | 1·346 | 1·77 | 74·9 | 71·3 | + 5 | 86·3 | + 21 |
| | 13·59 | 1·153 | 2·01 | 98·1 | 76·2 | + 29 | 108·3 | + 42 |
| | | | | | | 19 | | 39 |
| CN . | 17·74 | 1·136 | 2·21 | 115·4 | 130·9 | − 12 | 148·2 | + 13 |
| | 12·11 | 1·238 | 1·97 | 92·4 | 83·2 | + 11 | 110·0 | + 42 |
| | 16·21 | 1·170 | 2·06 | 101·3 | 85·2 | + 19 | 120·3 | + 41 |
| | | | | | | 14 | | 32 |
| CO . | 9·26 | 1·228 | 2·26 | 121·1 | 118·3 | + 3 | 243·2 | + 106 |
| | 12·17 | 1·193 | 2·18 | 112·5 | 99·5 | + 13 | 160·1 | + 61 |
| | 18·90 | 1·144 | 1·97 | 95·1 | 91·9 | + 4 | 99·7 | + 9 |
| | | | | | | 7 | | 59 |
| NO | 24·12 | 1·062 | 2·22 | 118·7 | — | — | 133·8 | — |
| | 4·72 | 1·449 | 1·70 | 69·4 | 55·7 | + 25 | 85·8 | + 54 |
| | 24·70 | 1·060 | 2·20 | 116·9 | 123·3 | − 6 | 130·2 | + 6 |
| | 15·91 | 1·138 | 2·26 | 120·6 | 107·8 | + 12 | 137·3 | + 28 |
| | | | | | | 14 | | 29 |
| $N_2^+$ | 23·95 | 1·051 | 2·67 | 170·9 | 146·6 | + 17 | 394·0 | + 169 |
| | 19·97 | 1·131 | 2·27 | 121·6 | 112·3 | + 8 | 167·0 | + 48 |
| | | | | | | 13 | | 108 |
| $O_2^+$ | 3·79 | 1·443 | 1·87 | 82·9 | 109·6 | − 24 | 142·6 | + 30 |
| | 16·51 | 1·117 | 2·18 | 113·1 | 132·2 | − 15 | 135·8 | + 3 |
| | | | | | | 20 | | 17 |
| $CO^+$ | 11·93 | 1·162 | 2·34 | 129·9 | 166·9 | − 22 | 234·2 | + 40 |
| | 9·84 | 1·253 | 1·97 | 91·8 | 96·5 | − 5 | 113·1 | + 17 |
| | 19·68 | 1·093 | 2·24 | 119·4 | 104 | + 15 | 146·0 | + 40 |
| | | | | | | 15 | | 32 |

It will be observed that for all the molecules except $Li_2$ and $O_2$, the values of $\mu\omega_e x_e$ are reproduced much better by the present function than by the Morse function. The mean percentage error over the states considered is 46 for the Morse function and for the reciprocal-exponential function only 16, showing that this function provides a very considerable improvement.

### (c) Calculation of $\omega_e x_e$ and $D$ from $k$ and $r_e$.

This is included because it is the one that might be of value for polyatomic molecules in which sometimes the only quantities available for the different linkages are the vibration frequency and the equilibrium distance. The results are summarised in Table III, the values of $a$ that are used are the same as in the first two tests.

The mean percentage error in the calculated values of $\mu \,.\, \omega_e x_e$ is 18. This is only slightly poorer than when the calculation uses $k$ and $D$ as the starting-points. The results are still very much better than those obtained using the Morse function. The calculated values of $D$ are not so good, the mean percentage error being about 28. This is much better agreement than is obtained with the Morse function which has been used by some workers for estimating dissociation energies. The difficulty lies in the fact that the calculated value of $D$ is determined by the magnitude of $m - nr_e$, and, since $nr_e$ is usually not very different from three, small changes in $nr_e$ lead to large changes in the results calculated for $D$. The percentage errors in $\mu \,.\, \omega_e x_e$ and $D$, on the whole, tend to be smaller for molecules containing atoms of higher atomic number. This is clearly demonstrated by comparing the results for $Li_2$ and $O_2$ in Table III.

To summarise, it may be said the function is only a little more satisfactory than the Morse function for the calculation of $D$ and is of little use for the accurate determination of $D$ from $k$ and $r_e$. However, it may be used to estimate the approximate magnitude of $\mu \,.\, \omega_e x_e$ from observed values of $k$ and $r_e$ and for this purpose might prove useful if applied to linkages in polyatomic molecules.

## Discussion.

### The Constant $a$.

It is interesting to examine more closely the values of $a$, particularly for those molecules involving C, N and O atoms. The data for molecules involving Li, Be, B and F are so scarce that no co-ordination of the results can be attempted. For the molecules formed from N, C and O atoms the six possible uncharged diatomic molecules and three of those which carry a single positive charge have been studied.

The constant $a$ measures the energy of repulsion of the two atoms when the separation between the nuclei is 1 A. This will presumably be larger the greater is the inter-penetration of the two electron clouds at this separation. This inter-penetration will be expected to decrease (i) the fewer electrons there are in the molecule, and (ii) the larger are the charges on the nuclei, since the increased charge will tend to draw the electron clouds into the nuclei. In support of (i) there are the following figures: $a_{CO} = 7{\cdot}0 \times 10^5$, $a_{CO^+} = 6{\cdot}6 \times 10^5$; and

$$a_{OO} = 6{\cdot}4 \times 10^5,\ a_{OO^+} = 6{\cdot}1 \times 10^5.$$

In both cases the value of $a$ for the charged molecule is 0·95 times the value for the uncharged molecule, which contains one more electron. However, in contrast to this, $a_{NN} = 7{\cdot}6 \times 10^5$ and $a_{NN^+} = 8{\cdot}6 \times 10^5$. Consideration of the series $C_2$, $N_2$ and $O_2$ indicates that the value of $a$ for

$N_2$ is not greatly in error, so the value of $a_{NN^+}$ is probably incorrect. If $a_{NN^+} = 7{\cdot}2 \times 10^5$ ($0{\cdot}95 \times 7{\cdot}6 \times 10^5$) is used, calculations from the observed values of $k$ and $r_e$ give for the two states of $N_2^+$ : $^2\Sigma_u$ : $\mu . \omega_e x_e = 123{\cdot}3$ (obs. 146·6), $D = 13{\cdot}54 \times 10^4$ (obs. $5{\cdot}10 \times 10^4$); $^2\Sigma_g^+$ : $\mu\omega_e x_e = 112{\cdot}9$ (obs. 112·3), $D = 12{\cdot}76 \times 10^4$ (obs. $10{\cdot}03 \times 10^4$). The agreement for $\mu . \omega_e x_e$ is a little improved by using the new value of $a$. For the lower state, $^2\Sigma_g^+$, the calculated value of $D$ is as close as can be expected to the observed value, but for the upper state the discrepancy is very great, and it may be that this dissociation energy is

TABLE III.—CALCULATION OF $\mu . \omega_e x_e$ AND $D$ FROM $k$ AND $r_e$.

| Mol. | $k$ (obs.) $\times 10^{-5}$. | $r_e$ (obs.). | $nr_e$ (calc.). | $\mu . \omega_e x_e$ (calc.). | $\mu . \omega_e x_e$ (obs.). | % Error. | $D$ (calc.). | $D$ (obs.). | % Error. |
|---|---|---|---|---|---|---|---|---|---|
| $Li_2$ . | 0·151 | 2·931 | 2·056 | 12·4 | 21·9 | − 44 | 1·02 | 0·73 | + 40 |
| | 0·131 | 3·11 | 1·730 | 9·32 | 5·25 | + 77 | 1·37 | 1·99 | − 32 |
| | 0·253 | 2·67 | 1·957 | 14·5 | 18·13 | − 20 | 1·57 | 1·82 | − 20 |
| $C_2$ . | 11·30 | 1·261 | 2·570 | 98·2 | 116·1 | − 16 | 7·01 | 4·94 | + 41 |
| | 9·10 | 1·315 | 2·580 | 91·0 | 72·6 | + 25 | 6·01 | 5·41 | + 9 |
| | 9·48 | 1·308 | 2·561 | 90·6 | 70·0 | + 29 | 6·44 | 8·76 | − 26 |
| $N_2$ . | 17·19 | 1·144 | 2·523 | 112·3 | 184·8 | − 39 | 9·60 | 3·65 | + 163 |
| | 12·32 | 1·207 | 2·617 | 111·2 | 101·1 | + 10 | 6·33 | 7·60 | − 17 |
| | 8·75 | 1·290 | 2·564 | 93·3 | 97·5 | − 4 | 6·02 | 5·67 | + 6 |
| | 22·82 | 1·094 | 2·430 | 117·5 | 101·1 | + 16 | 13·61 | 11·70 | + 16 |
| $O_2$ . | 2·36 | 1·599 | 2·714 | 68·1 | 85·7 | − 20 | 1·65 | 1·51 | + 9 |
| | 9·63 | 1·223 | 2·628 | 109·1 | 111·4 | − 2 | 4·95 | 5·55 | − 11 |
| | 11·75 | 1·204 | 2·452 | 98·6 | 95·9 | + 3 | 8·20 | 8·11 | + 1 |
| BeF . | 4·92 | 1·390 | 2·228 | 63·6 | 53·6 | + 19 | 6·19 | 3·03 | + 104 |
| | 5·73 | 1·357 | 2·169 | 64·0 | 55·7 | + 13 | 7·36 | 9·56 | − 23 |
| BO . | 6·26 | 1·301 | 2·587 | 93·6 | 65·7 | + 43 | 3·99 | 5·2 | + 23 |
| | 6·07 | 1·348 | 2·362 | 73·8 | 71·3 | + 3 | 6·07 | 5·89 | + 3 |
| | 13·59 | 1·199 | 1·957 | 72·0 | 76·2 | − 5 | 17·0 | 10·51 | + 62 |
| CN . | 17·74 | 1·148 | 2·429 | 106·7 | 130·9 | − 18 | 11·65 | 10·03 | + 16 |
| | 12·11 | 1·236 | 2·448 | 93·3 | 83·2 | + 12 | 8·96 | 9·14 | − 2 |
| | 16·21 | 1·169 | 2·426 | 102·6 | 85·1 | + 20 | 11·10 | 11·29 | + 2 |
| CO . | 9·25 | 1·232 | 2·750 | 118·3 | 118·0 | 0 | 3·40 | 3·19 | + 7 |
| | 12·17 | 1·205 | 2·529 | 104·1 | 99·5 | + 5 | 7·46 | 6·37 | + 15 |
| | 18·92 | 1·128 | 2·356 | 105·0 | 91·9 | + 14 | 13·34 | 15·9 | − 16 |
| NO . | 4·72 | 1·413 | 2·658 | 83·5 | 55·7 | + 50 | 3·01 | 4·60 | − 33 |
| | 24·70 | 1·060 | 2·331 | 117·0 | 123·3 | − 5 | 15·90 | 15·9 | 0 |
| | 15·91 | 1·146 | 2·412 | 105·7 | 107·9 | − 2 | 10·71 | 9·71 | + 10 |
| $N_2^+$ . | 23·95 | 1·071 | 2·691 | 149·1 | 146·6 | + 2 | 8·04 | 5·10 | + 60 |
| | 19·97 | 1·113 | 2·679 | 136·7 | 112·3 | + 22 | 7·31 | 10·03 | − 27 |
| $O_2^+$ . | 3·79 | 1·41 | 2·846 | 98·8 | 109·6 | − 10 | 1·18 | 2·23 | − 47 |
| | 16·51 | 1·14 | 2·263 | 96·7 | 132·2 | − 27 | 13·41 | 10·2 | + 31 |
| $CO^+$ . | 11·93 | 1·168 | 2·690 | 125·2 | 166·9 | − 25 | 4·77 | 4·27 | + 12 |
| | 9·84 | 1·212 | 2·700 | 117·2 | 96·5 | + 22 | 4·12 | 7·30 | − 43 |
| | 19·68 | 1·114 | 2·296 | 103·6 | 104 | 0 | 14·64 | 11·3 | + 30 |

incorrect and should be greater than $5{\cdot}10 \times 10^4$ A. ergs. In support of (ii) above, there are the following figures: $a_{NO} = 6{\cdot}6 \times 10^5$, $a_{OO^+} = 6{\cdot}1 \times 10^5$; and $a_{CN} = 7{\cdot}5 \times 10^5$, $a_{CO^+} = 6{\cdot}6 \times 10^5$. In the first case the ratio in the values of $a$ is 0·92 and in the second 0·88. According to (ii) $a_{NN^+}$ should be less than $a_{CN}$. This again favours the value of about $7{\cdot}2 \times 10^5$ for $a_{NN^+}$ instead of $8{\cdot}6 \times 10^5$, though a figure rather lower than 7·2 might have been expected.

Empirically it is observed that, for the uncharged molecules formed from C, N and O atoms, the following relation holds quite exactly:

$$a_{AB} = 0{\cdot}94\,\frac{a_{AA} + a_{BB}}{2}.$$

That is, the repulsion term for AB is smaller than the mean of those of AA and BB.

The values of $a$ for $C_2$, $N_2$ and $O_2$ ($8{\cdot}4$, $7{\cdot}6$ and $6{\cdot}4 \times 10^5$) fall into a series unlike, for instance, the interatomic distances for the ground states of these molecules. The decrease in $a$ on passing from $C_2$ to $O_2$ shows that the effect of the increasing charge on the nuclei more than compensates the increasing number of electrons, the electron clouds of the two atoms shrinking into the nuclei.

The regularities in the changes in $a$, and the fact that these changes occur in directions that would have been predicted, provide additional evidence for the essential correctness of this reciprocal-exponential function.

From the results of the tests described above, it is concluded that the reciprocal-exponential function provides a better representation of the whole course of the potential energy curve than does any other function. This agreement is better for molecules in which both the component atoms have several electrons in the incompleted electron shell than for those in which one of the component atoms has only one or two electrons in this shell. Thus better agreement is obtained with $O_2$ and CO than with $Li_2$ and BeF, and even BO. This representation is particularly good if the observed values of $k$ and $D$ are used to fix the curve. However, it is less good if $k$ and $r_e$ or $k$ and $\omega_e x_e$ are used to fix the values of the adjustable constants, the biggest discrepancy then being in the value of $D$.

## Summary.

The relative advantages of several functions relating the potential energy and the distance between two bonded atoms have been discussed. The function

$$V = \frac{a}{r^m} - b\,.\,e^{-nr}$$

has been examined in detail and expressions have been obtained from this function inter-relating the observable values of the quantities: $k$, $r_e$, $D$ and $\omega_e x_e$.

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# A THERMODYNAMIC STUDY OF BIVALENT METAL HALIDES IN AQUEOUS SOLUTION. PART V. THE ACTIVITY COEFFICIENTS OF CADMIUM CHLORIDE AND BROMIDE AT 25°.

By R. A. Robinson.[1]

*Received 30th July*, 1940.

Four determinations of the activity coefficient of cadmium chloride have been made by e.m.f. methods ; Horsch [2] made measurements over the range 0·0005 to 0·1 M. and a single measurement at 6·62 M.; Lucasse[3] covered the range 0·01 to 6 M. and Quintin[4] the range 0·001 to 0·05 M.; Harned and Fitzgerald,[5] who were concerned with the extrapolation of the standard potential of cadmium, made numerous measurements between 0·0005 and 0·1 M. and a few measurements up to 1 M. Whilst there is good agreement between the results of these four investigations in the concentration range up to 0·1 M., the data of Lucasse [3] and of Harned and Fitzgerald [5] do not agree between 0·1 and 1·0 M., the divergence increasing with the concentration. Isopiestic measurements have now been made on cadmium chloride solutions between 0·1 and 6 M. and the data of Lucasse have been confirmed with excellent agreement between his e.m.f. results and the present isopiestic data. Good agreement is also obtained with the determination of Horsch at the saturation point.

TABLE I.

**Cadmium Chloride.**

| | | | |
|---|---|---|---|
| 0·1060, 0·1054 ; | 0·1085, 0·1092 ; | 0·1184, 0·1180 ; | 0·1596, 0·1531 ; |
| 0·2002, 0·1870 ; | 0·2055, 0·1925 ; | 0·2908, 0·2597 ; | 0·3487, 0·3062 ; |
| 0·4285, 0·3680 ; | 0·4738, 0·4021 ; | 0·5778, 0·4758 ; | 0·6643, 0·5366 ; |
| 0·7262, 0·5836 ; | 0·8772, 0·6815 | 0·9078, 0·7099 ; | 0·9990, 0·7642 ; |
| 1·218, 0·9120 ; | 1·408, 1·033 ; | 1·452, 1·065 ; | 1·772, 1·282 ; |
| 1·818, 1·308 ; | 1·921, 1·371 ; | 2·120, 1·509 ; | 2·182, 1·551 ; |
| 2·201, 1·564 ; | 2·427, 1·723 ; | 2·490, 1·771 , | 2·710, 1·925 ; |
| 3·273, 2·334 ; | 3·327, 2·383 ; | 3·413, 2·449 ; | 3·754, 2·714 ; |
| 4·101, 3·009 ; | 4·298, 3·162 ; | 4·762, 3·554 ; | 5·331, 4·068 ; |
| 5·522, 4·241 ; | 5·847, 4·541 ; | 5·993, 4·688. | |

**Cadmium Bromide.**

| | | | |
|---|---|---|---|
| 0·1065, 0·1017 ; | 0·1261, 0·1187 ; | 0·1457, 0·1338 ; | 0·2205, 0·1903 ; |
| 0·2965, 0·2459 ; | 0·3897, 0·3112 ; | 0·4563, 0·3583 ; | 0·6634, 0·4975 ; |
| 0·8097, 0·6037 ; | 0·8924, 0·6615 ; | 0·9710, 0·7122 ; | 1·160, 0·8504 ; |
| 1·437, 1·070 ; | 1·558, 1·168 ; | 1·884, 1·433 ; | 2·097, 1·617 ; |
| 2·192, 1·709 ; | 2·285, 1·788 ; | 2·306, 1·811 ; | 2·515, 2·004 ; |
| 2·792, 2·263 ; | 2·984, 2·446 ; | 3·261, 2·717 ; | 3·418, 2·883 ; |
| 3·639, 3·100 ; | 3·758, 3·224 ; | 3·844, 3·314 ; | 4·062, 3·530 ; |
| 4·064, 3·536. | | | |

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[1] Sterling Fellow, Yale University, 1940.

[2] *J. Amer. Chem. Soc.*, 1919, **41**, 1787.

[3] *Ibid.*, 1929, **51**, 2597.

[4] *Compt. rend.*, 1935, **200**, 1754.

[5] *J. Amer. Chem. Soc.*, 1936, **58**, 2624.

Cadmium bromide has been investigated by Lucasse[3] and Bates,[6] using the e.m.f. method; the two sets of results are in reasonable agreement. Isopiestic measurements have been made on this salt but the method, which worked very well with cadmium chloride, proved more difficult to apply to the bromide at concentrations less than 0·5 M. The difficulty is probably due to hydrolysis of the salt, and is much more marked in the case of zinc bromide. Numerous attempts have been made to obtain the activity coefficient of the latter salt by the isopiestic method but without success. For this reason the present determination on cadmium bromide can only be presented as affording support for the data of Lucasse and Bates; on the other hand, the measurements on cadmium chloride are believed to be sufficiently good to rank as an independent determination.

TABLE II.

Activity Coefficients of Cadmium Halides at 25°.

| *m.* | $CdCl_2$. | $CdBr_2$. | $CdI_2$ |
|---|---|---|---|
| 0·1 | (0·228) | 0·190 | 0·1074 |
| 0·2 | 0·1632 | (0·132) | (0·0685) |
| 0·3 | 0·1324 | 0·105 | 0·0523 |
| 0·4 | 0·1133 | 0·0895 | 0·0433 |
| 0·5 | 0·1001 | 0·0784 | 0·0377 |
| 0·6 | 0·0902 | 0·0702 | 0·0337 |
| 0·7 | 0·0825 | 0·0640 | 0·0307 |
| 0·8 | 0·0758 | 0·0594 | 0·0284 |
| 0·9 | 0·0708 | 0·0553 | 0·0266 |
| 1 | 0·0664 | 0·0521 | 0·0251 |
| 1·5 | 0·0523 | 0·0418 | 0·0205 |
| 2 | 0·0439 | 0·0363 | 0·0181 |
| 2·5 | 0·0384 | 0·0329 | — |
| 3 | 0·0351 | 0·0307 | — |
| 3·5 | 0·0322 | 0·0292 | — |
| 4 | 0·0304 | 0·0280 | — |
| 4·5 | 0·0290 | — | — |
| 5 | 0·0278 | — | — |
| 5·5 | 0·0269 | — | — |
| 6 | 0·0263 | — | — |

## Experimental.

Table I records the molalities of isopiestic solutions, that of the reference solution, potassium chloride, being given by the second of each pair of figures. The activity coefficients, calculated relative to those of potassium chloride previously recorded,[7] are given in Table II, together with the data for cadmium iodide.[8]

The activity coefficients are very low compared with those more normal bivalent metal halides which can probably be classified as strong electrolytes; of this group barium chloride exhibits the lowest activity coefficient with a minimum value of 0·384 at 0·7 M. Complex ion formation appears to be established in the case of cadmium iodide and from the nature of the activity coefficient curves this must be almost equally operative in the case of the chloride and bromide. The three activity coefficient curves place themselves regularly in the order $CdCl_2 > CdBr_2 > CdI_2$, but the corresponding osmotic coefficient curves are more complex, the order being $CdCl_2 > CdBr_2 > CdI_2$ below 1·4 M. and the reverse of this order above 2 M.

## Summary.

The activity coefficients of cadmium chloride and bromide have been determined at 25°.

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[6] *J. Amer. Chem. Soc.*, 1939, **61**, 308.
[7] Robinson, *Trans. Faraday Soc.*, 1939, **35**, 1217.
[8] Robinson and Wilson, *ibid.*, 1940, **36**, 738.

# PART VI. THE ACTIVITY COEFFICIENTS OF MANGANESE, COBALT, NICKEL AND COPPER CHLORIDE IN AQUEOUS SOLUTION AT 25°.

By R. A. Robinson[1] and R. H. Stokes.

The activity coefficient of cobalt chloride[2] is intermediate between that of calcium chloride and magnesium chloride, indicating that it belongs to the class of highly dissociated bivalent metal chlorides; in contrast to this salt zinc chloride[3] has a very low activity coefficient in concentrated solution consistent with intermediate and possibly complex ion formation. It is therefore of interest to examine some other chlorides of metals in this transition group.

## Experimental.

The solutions recorded in Table I were found to be isopiestic, the second of each pair of figures indicating the molality of the reference salt, potassium chloride. The copper chloride solutions were contained in platinum dishes, the other solutions in silver dishes.

TABLE I.

**Manganese Chloride.**

0·1148, 0·1596; 0·1463, 0·2044; 0·2276, 0·3248; 0·2937, 0·4251;
0·4537, 0·6801; 0·6091, 0·9450; 0·9826, 1·660; 1·259, 2·236;
1·329, 2·396; 1·539, 2·868; 1·601, 3·000; 1·966, 3·860;
2·306, 4·662; 2·353, 4·782.

**Nickel Chloride.**

0·1188, 0·1662; 0·1975, 0·2820; 0·2158, 0·3113; 0·5380, 0·8482;
0·7864, 1·328; 0·9430, 1·661; 1·212, 2·284; 1·443, 2·872;
1·831, 3·942; 2·123, 4·81.

**Cupric Chloride.**

0·1085, 0·1495; 0·1128, 0·1558; 0·2048, 0·2838; 0·2474, 0·3462;
0·2516, 0·3521; 0·3998, 0·5750; 0·5334, 0·7856; 0·6555, 0·9860;
0·7236, 1·107; 0·8388, 1·300; 0·9378, 1·472; 1·054, 1·677;
1·206, 1·945; 1·259, 2·035; 1·297, 2·105; 1·328, 2·157;
1·481, 2·430; 1·553, 2·574; 1·847, 3·106; 1·996, 3·366;
2·111, 3·577; 2·415, 4·121; 2·530, 4·314; 2·652, 4·522;
2·769, 4·729.

From these measurements activity coefficients were evaluated with reference to the activity coefficients of potassium chloride recorded previously.[4] In an earlier paper[2] activity coefficients for cobalt chloride were given relative to $\gamma = 0·570$ at 0·05 M. Now that isopiestic results are available for more salts of this type, it appears from a comparison of the isopiestic ratios at low concentrations that a more probable reference value would be $\gamma = 0·526$ at 0·1 M. In Table II are given the activity coefficients of cobalt chloride recomputed on this basis.

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[1] Sterling Fellow, Yale University, 1940.

[2] Robinson, *Trans. Faraday Soc.*, 1938, **34**, 1142.

[3] Robinson and Stokes, *ibid.*, 1940, **36**, 733.

[4] Robinson, *ibid.*, 1939, **35**, 1217.

No data are available with which to compare the results for manganese, cobalt and nickel chloride. Redlich and Rosenfeld[5] have made an estimate of the activity coefficient of cupric chloride which agrees with the values now obtained within 0·005 up to 1 M., but shows considerable divergence at 2 and 3 M.

The three salts, manganese, cobalt and nickel chloride have activity coefficients of the magnitude of calcium chloride, decreasing in the order: $NiCl_2 > CoCl_2 > MnCl_2$. Copper chloride is out of place in this series, its activity coefficient being comparable with that of barium chloride. Since magnesium, calcium, strontium, manganese, nickel and cobalt chloride form hexahydrates in the solid state, whereas copper and barium chloride form dihydrates, the low values of the activity coefficient of copper chloride may be associated with the lower amount of water co-ordinated with the ion in solution, and hence with a lower "ionic diameter." The next member of the series, zinc chloride, has a somewhat larger "ionic diameter" of 5 A., according to e.m.f. data at high dilutions,[3] and in the solid state can accommodate a maximum of four molecules of water of crystallisation. In dilute solution (< 0·4 M.) its activity coefficient is intermediate between copper chloride and strontium chloride but at higher concentrations its behaviour is complicated by the formation of intermediate or complex ions.

TABLE II.

ACTIVITY COEFFICIENTS OF MANGANESE, COBALT, NICKEL AND CUPRIC CHLORIDE AT 25°.

| m. | $MnCl_2$. | $CoCl_2$. | $NiCl_2$. | $CuCl_2$. |
|---|---|---|---|---|
| 0·1 | 0·522 | 0·526 | 0·526 | 0·501 |
| 0·2 | 0·474 | 0·482 | 0·483 | 0·447 |
| 0·3 | 0·454 | 0·466 | 0·468 | 0·423 |
| 0·4 | 0·446 | 0·463 | 0·465 | 0·409 |
| 0·5 | 0·446 | 0·465 | 0·468 | 0·405 |
| 0·6 | 0·448 | 0·473 | 0·476 | 0·403 |
| 0·7 | 0·455 | 0·483 | 0·489 | 0·403 |
| 0·8 | 0·463 | 0·496 | 0·504 | 0·405 |
| 0·9 | 0·474 | 0·514 | 0·522 | 0·408 |
| 1·0 | 0·486 | 0·533 | 0·542 | 0·411 |
| 1·2 | 0·516 | 0·578 | 0·595 | 0·419 |
| 1·4 | 0·554 | 0·635 | 0·660 | 0·430 |
| 1·6 | 0·596 | 0·706 | 0·737 | 0·442 |
| 1·8 | 0·637 | 0·785 | 0·826 | 0·454 |
| 2·0 | 0·682 | 0·884 | 0·935 | 0·466 |
| 2·2 | 0·732 | — | — | 0·478 |
| 2·4 | — | — | — | 0·489 |
| 2·6 | — | — | — | 0·500 |
| 2·8 | — | — | — | 0·512 |

## Summary.

Data are presented for the activity coefficients of manganese, nickel, cobalt and copper chloride in aqueous solution at 25°.

*Yale University,*
*New Haven, Conn.*

*Auckland University College,*
*New Zealand.*

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[5] Landolt-Börnstein, "*Tabellen*," 3er *Ergänz.*, 2143.

# THE TRANSPORT NUMBERS OF ZINC CHLORIDE FROM E.M.F. MEASUREMENTS.

By A. C. Harris and H. N. Parton.

*Received 22nd August*, 1940.

Hittorf[1] found that the cation transport number of aqueous solutions of $ZnCl_2$ is negative in strong solutions above 2 M. Parton and Mitchell[2] have studied the variation of the transport number of $ZnBr_2$ with concentration at 25° C. by cells with and without liquid junction, and have shown that the cation transport number $T_C$ becomes negative in solutions above 2·7 M. A similar study of $ZnCl_2$ solutions is reported here.

## Experimental.

Sticks of A.R. $ZnCl_2$ were dissolved in water, the precipitate of oxychloride dissolved by addition of HCl, and the resulting solution analysed for Zn and Cl. Sufficient ZnO was then added to produce equivalence of the two ions. The resulting solution did not precipitate oxychloride on dilution, and consequently each dilution was analysed for Zn only. The Zn analysis was by titration with potassium ferrocyanide with diphenylbenzidine as indicator. The AgCl electrodes were of the type described by Carmody,[3] and the Zn electrodes were amalgamated rods. They were unaffected by oxygen at the electrolyte concentrations used. The cell with liquid junction was of the type used by Lucasse,[4] with a static boundary, and an H vessel was used for the cell without liquid junction.

## Experimental Results.

In Table I the complete data are given in round molalities (mols. per 1000 g. of water) obtained from a large scale plot of the experimental voltages for the two types of cell against log $m$. The first column gives the molalities, the second, $E_1$, the E.M.F. of the corresponding cell without liquid junction, and the third the activity coefficients calculated as described below. The fourth column, $E_t$, gives the E.M.F. of the cell with transport, and the fifth, $E'_t$, the E.M.F. calculated from the equations discussed below. The sixth column, $\Delta$, gives the difference in millivolts between $E_t$ and $E'_t$, and the seventh gives the transport numbers. Data are given for 25° C. and 35° C.

## The Activity Coefficients.

The activity coefficients were calculated from the equation

$$E = E^\circ - \frac{RT}{2F} \log 4m^3f^3,$$

the values of $E^\circ$ used being 0·9851 at 25° C. and 0·9774 at 35° C., these being obtained from the standard potentials of the Zn electrode given

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[1] Hittorf, *Z. physik. Chem.*, 1903, **43**, 249.

[2] Parton and Mitchell, *Trans. Faraday Soc.*, 1939, **35**, 758.

[3] Carmody, *J.A.C.S.*, 1929, **51**, 2901.

[4] Lucasse, *ibid.*, 1925, **47**, 743.

TABLE I.

25° C.

| $m$. | $E_1$. | $f$. | $E_t$. | $E'_t$. | $\Delta$(mv). | $T_C$. |
|---|---|---|---|---|---|---|
| 0·50 | 1·0293 | 0·400 | + 0·0048 | + 0·0047 | + 0·1 | 0·331 |
| 0·70 | 1·0180 | 0·383 | + 0·0083 | + 0·0079 | + 0·4 | 0·249 |
| 0·90 | 1·0110 | 0·358 | + 0·0096 | + 0·0096 | 0·0 | 0·194 |
| 1·00 | 1·0080 | 0·348 | + 0·0100 | + 0·0100 | 0·0 | 0·171 |
| 2·00 | 0·9874 | 0·297 | + 0·0117 | + 0·0118 | − 0·1 | 0·000 |
| 3·00 | 0·9721 | 0·294 | + 0·0104 | + 0·0107 | − 0·3 | − 0·137 |
| 4·00 | 0·9582 | 0·317 | + 0·0075 | + 0·0080 | − 0·5 | − 0·256 |
| 5·00 | 0·9445 | 0·361 | + 0·0032 | + 0·0037 | − 0·5 | − 0·364 |
| 6·00 | 0·9312 | 0·425 | − 0·0019 | − 0·0013 | − 0·6 | − 0·456 |
| 7·00 | 0·9194 | 0·495 | − 0·0077 | − 0·0075 | − 0·2 | − 0·524 |
| 8·00 | 0·9068 | 0·601 | − 0·0137 | − 0·0139 | + 0·2 | − 0·562 |
| 9·00 | 0·8954 | 0·718 | − 0·0193 | − 0·0188 | − 0·5 | − 0·593 |
| 10·00 | 0·8850 | 0·846 | − 0·0246 | − 0·0245 | − 0·1 | − 0·559 |
| 11·00 | 0·8755 | 0·986 | − 0·0298 | − 0·0298 | 0 | − 0·548 |
| 12·00 | 0·8667 | 1·135 | − 0·0350 | − 0·0345 | − 0·5 | − 0·522 |
| 35° C. | | | | | | |
| 0·50 | 1·0268 | 0·364 | + 0·0034 | + 0·0035 | − 0·1 | 0·358 |
| 0·70 | 1·0174 | 0·330 | + 0·0062 | + 0·0065 | − 0·3 | 0·285 |
| 0·90 | 1·0101 | 0·308 | + 0·0082 | + 0·0083 | − 0·1 | 0·219 |
| 1·00 | 1·0072 | 0·298 | + 0·0091 | + 0·0089 | + 0·2 | 0·194 |
| 2·00 | 0·9873 | 0·246 | + 0·0109 | + 0·0109 | 0 | 0·000 |
| 3·00 | 0·9710 | 0·247 | + 0·0096 | + 0·0096 | 0 | − 0·160 |
| 4·00 | 0·9562 | 0·268 | + 0·0064 | + 0·0063 | + 0·1 | − 0·293 |
| 5·00 | 0·9416 | 0·310 | + 0·0018 | + 0·0016 | + 0·2 | − 0·373 |
| 6·00 | 0·9266 | 0·376 | − 0·0045 | − 0·0044 | − 0·1 | − 0·437 |
| 7·00 | 0·9135 | 0·448 | − 0·0103 | − 0·0101 | − 0·2 | − 0·453 |
| 8·00 | 0·9011 | 0·535 | − 0·0167 | − 0·0170 | + 0·3 | − 0·460 |
| 9·00 | 0·8902 | 0·625 | − 0·0222 | − 0·0216 | + 0·6 | − 0·402 |

by Bates,[5] and of the AgCl electrode by Harned and Ehlers.[6] The minimum value of the activity coefficient occurs at about 2·6 M at both temperatures, as compared with 0·6 M for the bromide,[2] and 0·25 M for the iodide [5] at 25° C. Minima were found by Foxton and Shutt [7] at about the same concentration for zinc chloride at 60° and 80° C.

### The Transport Numbers.

The cells measured were

$$Zn_xHg/ZnCl_2(m)/AgCl(s)/Ag \qquad . \quad . \quad . \quad (1)$$

and

$$Ag/AgCl(s)/ZnCl_2(m_1)/ZnCl_2(m_2)/AgCl(s)/Ag \qquad . \quad . \quad (2)$$

The E.M.F. of cell (2) with liquid junction is given by

$$E_t = \frac{3RT}{2F} \,.\, T_C \,.\, \ln \frac{m_1 f_1}{m_2 f_2}.$$

At 25° C. the molality $m_1$ was kept constant at 0·3334, and at 35° C. at 0·3273.

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[5] Bates, *J.A.C.S.*, 1938, 60, 2983.

[6] Harned and Ehlers, *ibid.*, 1933, 55, 2179.

[7] Foxton and Shutt, *Trans. Faraday Soc.*, 1927, 23, 480.

The corresponding cell without liquid junction is a combination of two cells of type (1), with solutions of concentration $m_1$ and $m_2$ respectively, and its E.M.F. is given by

$$E_1 = \frac{3RT}{2F} \ln \frac{m_1 f_1}{m_2 f_2}.$$

By interpolation the E.M.F. of cell (1) at 25° C. when $m = 0{\cdot}3334$ is 1·0425 volts, and at 35° C. for $m = 0{\cdot}3273$ is 1·0385 volts. The E.M.F.'s listed in the second column were subtracted from these values, and the resulting figures plotted against the corresponding values at $E_t$. The slope of this plot, which gives $T_C$, was obtained analytically. The curve obtained at 25° C. could be fitted by the following equation, the E.M.F.'s being in millivolts:—

$$E_t = 11{\cdot}7 - a(E_1 - 55{\cdot}1)^2 + b(E_1 - 55{\cdot}1)^4.$$

The constant $a$ had the following values: from 0·5$m$ to 2·0$m$, $a = 0{\cdot}0042$; from 2·0$m$ to 7·0$m$, $a = 0{\cdot}0045$; from 7·0$m$ to 9·0$m$, $a = 0{\cdot}0044$; from 9·0$m$ $a = 0{\cdot}0042$. The constant $b$ was $7 \times 10^{-8}$ over the whole range.

At 35° C. the curve was fitted by

$$E_t = 10{\cdot}9 - a(E_1 - 51{\cdot}2)^2 + b(E_1 - 51{\cdot}2)^4.$$

The values of $a$ were: 0·5$m$ — 4·0$m$, $a = 0{\cdot}0050$; 4·0$m$ — 7·0$m$, $a = 0{\cdot}0047$; 7·0$m$ — 9·0$m$, $a = 0{\cdot}0049$. The constant $b$ was $1{\cdot}5 \times 10^{-7}$ over the whole range. The cation transport numbers $T_C$ were obtained by differentiation of the equations in the usual way.

As in the case of $ZnBr_2$, the cation transport number becomes negative, in this case above 2$m$. Whereas for the bromide it becomes constant at about 11$m$, for the chloride a minimum is reached at about 9$m$ at 25° C., and about 8$m$ at 35° C. As in the case of the bromide, the conductance data of Rabinowitsch,[8] corrected for viscosity, also show a minimum, at 10$m$ at 25° C.

Hittorf obtained — 0·241 for $T_C$ in 4·035 molal $ZnCl_2$ solution, and — 0·08 at 2·64$m$ in fair agreement with the values which can be interpolated from the data of Table I, which are — 0·260 and — 0·088 respectively at 25° C.

A plot of $T_C$ against $m^{\frac{1}{2}}$ is very similar to that obtained with the bromide. Taking $l_{Zn^+}$ as 53·5[9] and $l_{Cl^-}$ as 76·3,[10] $T_C = 0{\cdot}412$ at infinite dilution at 25° C., and the limiting slope for $T_C$ against $C^{\frac{1}{2}}$ required by the interionic attraction theory is — 0·216. As with the bromide, the curve will approach this slope from above.

## Summary.

1. Measurements are reported of cells with and without liquid junction containing aqueous zinc chloride solutions from 0·5$m$ to 12$m$.

2. The activity coefficients and transport numbers of zinc chloride have been obtained.

We have much pleasure in thanking Dr. H. G. Denham for his interest in this work.

*Canterbury University College,*
*Christchurch, New Zealand.*

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[8] Rabinowitsch, *Z. physik. Chem.*, 1921, 98, 338.

[9] *Landolt-Börnstein Tabellen*, 2er *Ergänz.*, p. 2059.

[10] MacInnes, Shedlovsky and Longsworth, *J.A.C.S.*, 1932, 54, 2758.

# THE KINETICS OF THE THERMAL DECOMPOSITION OF GASEOUS SILICON TETRAETHYL AND SILICON TETRAPROPYL.*

By Chas. E. Waring.†

*Received 26th August*, 1940.

The modern theory of reaction mechanism in the gaseous phase would undoubtedly be aided by kinetic studies of the decomposition of a series of molecules in which there is a stepwise gradation of structure and stability. To some extent this has been done for some of the simpler hydrocarbons. It was thought that a study of a series consisting of more complicated type molecules might prove helpful. In this regard the tetra-alkals of the fourth group of the periodic table suggest themselves as interesting subjects for investigation. It might also be of interest to see what type of reaction is produced by compounds which might presumably be expected to split off alkyl radicals as a primary process.

Research on the thermal decomposition of tetra-alkyls has been confined to date to lead[1] and germanium,[2] tetraethyl, and silicon tetramethyl,[3] but no attempt has been made to study the effect of changing the alkyl radical on the same central atom. Since a beginning has been made with silicon tetramethyl, it was felt worth while in the present investigation to extend this series to include silicon tetraethyl and silicon tetrapropyl.

## Experimental.

The course of the decompositions was followed in the usual manometric method. The gas reacted in pyrex bulbs of 100 and 250 c.c. capacity, and by using small bore capillary tubing the dead space was reduced to about 2 per cent. of the total volume.

An electric furnace was maintained at constant temperature within a half degree by a special thermoregulator-mercury relay device. Temperatures were measured by a platinum-platinum-rhodium thermocouple which was regularly checked by a standard potentiometer. Since the normal boiling-points of these compounds were 151° ($Si(C_2H_5)_4$) and over 200°, all tubing and taps were heated electrically. The temperature of the taps did not vary more than 3° over a three-hour period. A special aluminium stearate tap grease was employed. The rest of the apparatus consisted of the usual system for attaining low pressures.

Silicon tetraethyl and tetrapropyl were prepared by a Grignard method suggested by Dr. George Calingert of the Ethyl Gas Corporation.‡ Each preparation was carefully fractionated under reduced pressure and only that product which had a constant boiling-point within ± 0·05° was used. Different preparations gave the same boiling-points within this limit after purification.

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* Presented at the Detroit Meeting of the American Chemical Society.

† Lalor Foundation Fellow, 1939-40, Balliol and Trinity Laboratory, Oxford.

‡ Private communication.

[1] Leermakers, *J.A.C.S.*, 1933, **55**, 4508.

[2] Geddes and Mack, *ibid.*, 1930, **52**, 4372.

[3] Helm and Mack, *ibid.*, 1937, **59**, 60.

The gaseous products were analysed on a Bone and Wheeler apparatus. The higher olefines were separated from the ethylene by the method of Hurd and Spence.[4]

## Silicon Tetraethyl.

### 1. Nature of the Decomposition.

From photochemical evidence with allied organo-metallic compounds, one might reasonably expect the primary step in the thermal decomposition of silicon tetraethyl to be

$$Si(C_2H_5)_4 = Si + 4(C_2H_5),$$
$$\text{or} \quad Si(C_2H_5)_4 = Si(C_2H_5)_3 + C_2H_5 \text{ (slow)},$$
$$Si(C_2H_5)_3 = Si + 3C_2H_5 \text{ (fast)}.$$

In a recent paper, Moore and Taylor[5] indicated the various possibilities of recombination and reaction that ethyl radicals may undergo. These authors considered, in the main, only the reactions of ethyl radicals produced photochemically, and at temperatures well below those employed thermally. Hence, in the present study, secondary reactions involving ethyl radicals may not necessarily result in the same final products of reaction. Thus, if ethyl radicals are initially produced in the thermal decomposition of silicon tetraethyl at high temperatures, these radicals may be expected to react rather rapidly and give rise to secondary reactions, which may tend to mask the primary step. Moreover, the hydrocarbons produced initially from these radicals may undergo further decomposition. This means that the relation of the primary and secondary change to the actual chemical reaction must be rather carefully thought out.

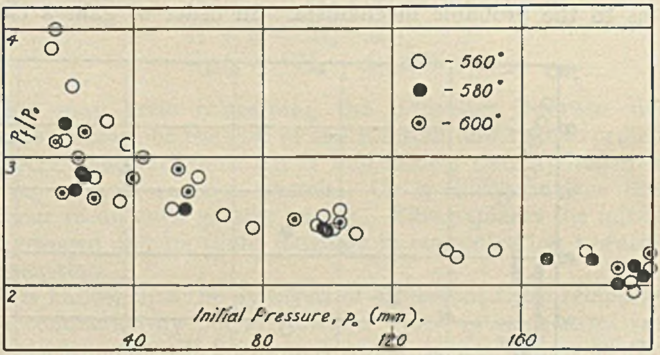

Fig. 1.—Variation of $P_f/P_0$ with $P_0$ for $Si(C_2H_5)_4$ at different temperatures.

The most convenient method of following this reaction is by the rate of pressure change. This procedure is straightforward enough for decompositions in which the initial products undergo no subsequent change, but may lead to erroneous conclusions in the event of complicating side reactions. Therefore, it is our plan to interpret our kinetic data in the light of analyses.

Silicon tetraethyl decomposes to give a total pressure increase of about two and one-half times that of the initial pressure. Fig. 1 shows that the ratio of the final to the initial pressure is not exactly constant

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[4] Hurd and Spence, *J.A.C.S.*, 1929, 51, 3353.

[5] Moore and Taylor, *J. Chem. Physics*, 1940, 8, 396.

and varies somewhat with the initial pressure. On the whole, the total pressure increase is greater at low initial pressures, and falls off asymptotically at higher pressures. The figure does indicate, however, that the end-points are not affected by temperature.

This lack of complete reproducibility in end-points obtained from the same initial pressures creates the problem of determining the best method of expressing the rate constant. From what has been said, it should be clear that a different value for the order of reaction might be obtained, depending whether the rates are determined on the basis of a given fraction of the initial pressure, or from the total pressure increase. Since there is a complex series of secondary reactions in the decomposition of silicon tetraethyl, and since it is the primary process that is of greater importance, we shall depend upon the initial rate. It will, however, be shown later that the result is substantially the same, no matter whether the order of reactions is obtained from the initial rate, or from the half-time for the total pressure increase.

## 2. Reaction Products.

The analyses of the final reaction products gave but little indication as to the probable mechanism. In order to gain a clearer picture of what was occurring during the primary stage, samples were withdrawn from the reaction vessel over the whole range of the decomposition. The results are shown in Fig. 2.

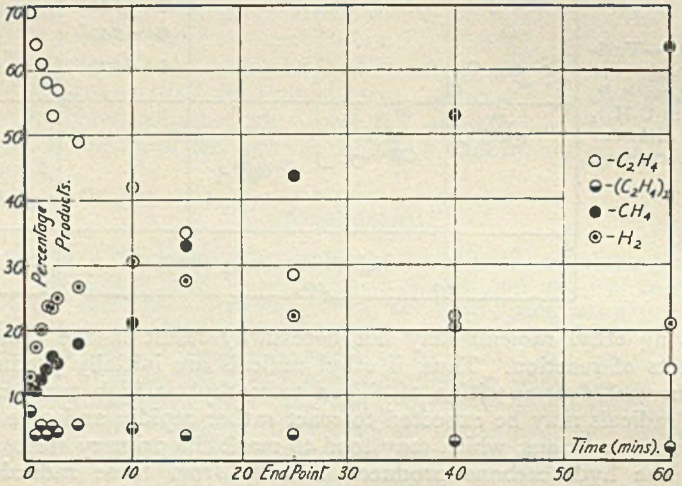

FIG. 2.—Showing the change in the decomposition products of $Si(C_2H_5)_4$ with time at 580° C. Each point is the average of five analyses.

The analyses indicate that the initial step in the reaction is the formation of ethyl radicals and silicon. These ethyl radicals then react to give ethylene and hydrogen and a very slight amount of higher olefines. The ethylene formed is slowly converted into methane and carbon. Although two ethyl radicals might unite to form butane, at 580° C. none was found. Since all the analyses gave a mean carbon atom value of 1·0 for the saturated hydrocarbons, it is concluded that the only one of any stability formed is methane. Undoubtedly, it is the slow subsequent conversion of ethylene which makes the end-points difficult to interpret, and gives added reason for basing the order of reaction upon the initial rates.

At 580° C. the decomposition is practically complete within twenty-five minutes. Up to within five minutes of the end-point, the only noticeable deposit on the walls of a new flask is a white coating of silicon. After runs have gone to completion the walls show the blackish-gray deposit, which eventually assumes the shiny-black appearance of carbon particles. Even after no further change in pressure occurs the ethylene concentration continues to decrease and the methane concentration to increase, which suggests a reaction of the type

$$C_2H_4 = CH_4 + C.$$

It is now possible to postulate the following mechanism as being the most predominant:—

Primary Process, $Si(C_2H_5)_4 = Si + 4C_2H_5,$
or, $Si(C_2H_5)_4 = Si(C_2H_5)_3 + C_2H_5$ (slow),
$Si(C_2H_5)_3 = Si + 3C_2H_5$ (fast).

Secondary Process $C_2H_5 = C_2H_4 + H,$
$H + H = H_2$ (fast),
$C_2H_4 = CH_4 + C$ (slow).

The question may arise concerning the difference between the observed pressure increase at the end of the reaction and that expected from stoichiometric considerations. It is well known that hydrogen is adsorbed on the walls of reaction vessels. On a silicon surface this process may occur to an even greater extent. This explains the initial deficiency of hydrogen and its slight decrease in concentration towards the end of the reaction.

Secondly, it is known that the pyrolysis of olefines at these temperatures can be accompanied by polymerisations which in some cases are catalytic, and condensates will be formed which do not appear in the gaseous products.

Polymerisation would be facilitated at higher rather than lower initial pressures, making the $P_f/P_0$ ratio greater in the latter case. Fig. 1 substantiates this and by extrapolating to zero pressure, a total pressure increase of about the right order of magnitude is obtained for the stoichiometric equation. Therefore, under the conditions of the experiments it is not surprising that the total pressure increase is somewhat smaller than that expected from a theoretical standpoint.

## 3. Order of Reaction.

Fig. 3 shows the change of pressure with time for various initial pressures, the increase in each case being expressed as a percentage of the initial pressure. Between 200 and about 50 mm. the pressure-time curves almost exactly coincide over the initial stage of the decomposition, which corresponds to the splitting off of ethyl radicals from the silicon atom. This reproducibility in the early stage indicates that the primary process, at least, is a first order reaction. Deviations which occur in the later stages need not interest us too much, as they relate to the secondary decompositions of the primary products, and over a wide pressure range do not influence the initial rate.

That the reaction is of the first order is further substantiated by Fig. 4, in which the reciprocal of the half life is plotted against the initial pressure. At one temperature, however, a plot of the logarithm of the half-time against the logarithm of the initial pressure, gave an order of reaction of 1·36. On the whole, it may be said that the decomposition of silicon tetraethyl is of an order which is predominately the first, although increasing slightly at lower initial pressures.

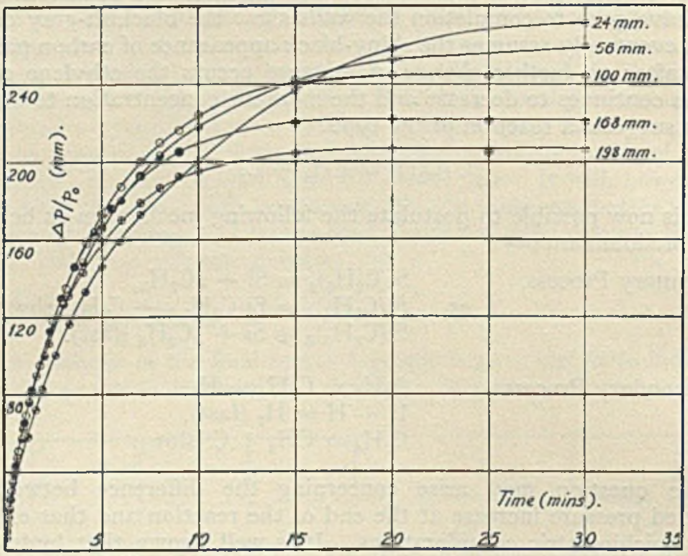

Fig. 3.—Pressure increase—time curves for several reactions at 580° C.—$Si(C_2H_5)_4$.

## 4. Effect of Nitric Oxide.

It is definitely known (Staveley and Hinshelwood,[6] Staveley,[7] and Hobbs and Hinshelwood [8]) that NO will markedly inhibit the rate of decomposition of ethane at 600° C. According to the theory of NO inhibition radicals which propagate chains are removed by reaction with

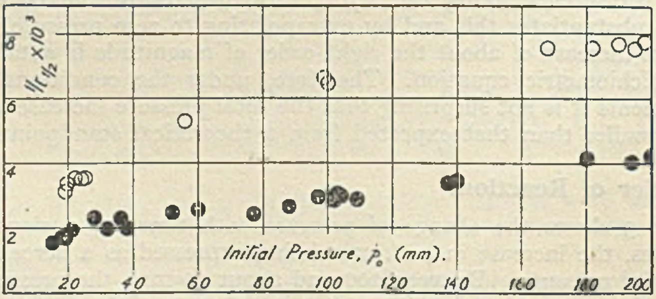

FIG. 4.—Black circles, 560° C.; white circles, 580° C.—$Si(C_2H_5)_4$.

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[6] Staveley and Hinshelwood, *Proc. Roy. Soc. A*, 1936, **154**, 335.

[7] Staveley, *ibid.*, 1937, **162**, 557.

[8] Hobbs and Hinshelwood, *ibid.*, 1938, **167**, 439.

the NO. Thus, an investigation of the decomposition of silicon tetraethyl in the presence of NO should be a test not only for the presence of ethyl radicals, but also an indication of the existence of reaction chains of any appreciable length.

It was found that small amounts of NO have no effect upon this reaction. Large amounts of NO affect the total pressure increase in a manner that is very marked in the secondary stages of the reaction, while the primary rate is affected only very slightly. A comparison between the inhibited and uninhibited reactions is given in Fig. 5.

The fact that NO does affect the initial rate—even though the effect is not great—indicates that radicals are present, which react with it. However, since the magnitude of this effect is so small it can be safely assumed that the reaction $Si(C_2H_5)_4$ + Radical = is not occurring to any great extent. Hence, the decomposition of silicon tetraethyl does not proceed by a chain mechanism.

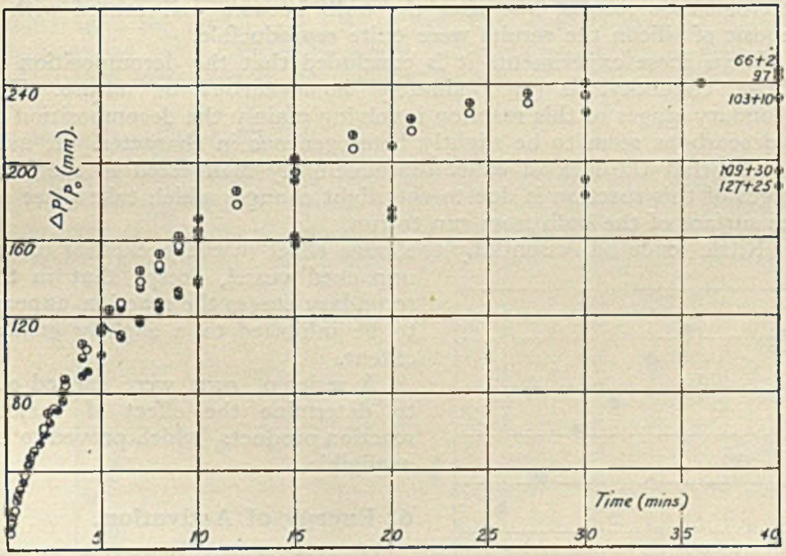

FIG. 5.—Inhibition by nitric oxide of the thermal decomposition of $Si(C_2H_5)_4$ at 560° C.; ⊙ $P_0 = 97$ mm. unihibited; ⊕ $P_0 = 66$ mm. + 2 mm. NO; ◒ $P_0 = 103$ mm. + 10 mm. NO; ⊘ $P_0 = 109$ mm. + 30 mm. NO; ● $P_0 = 127$ mm. + 25 mm. NO.

Since, however, ethyl radicals are formed in the primary process, the question arises as to their ultimate fate. They might recombine by simple binary collisions to form butane. However, at no stage of the reaction does analysis give evidence for this product. Although the possibility exists, on general grounds the removal of an ethyl radical by a hydrogen atom, in a simple binary process, is less likely. Since little or no ethane is formed this process cannot occur to any measurable extent.

It would appear, then, that the ethyl radicals formed in the initial break-up of $Si(C_2H_5)_4$ must disappear by reactions of which

$$C_2H_5 = C_2H_4 + H$$

becomes the predominant one. The hydrogen atoms so produced are converted into hydrogen molecules by homogeneous ternary collisions and/or reaction at the walls. In either case, this rate is fast, and has no effect upon the kinetics of the reaction as a whole. The possibility of reactions between hydrogen atoms and unsaturated hydrocarbons are not excluded but do not assume an important rôle in this particular reaction.

### 5. Surface Effects.

Experiments in a packed reaction vessel having a surface/volume ratio of 10 times over that of the unpacked bulb showed that at three different temperatures the initial rate remained unchanged. The secondary stages of the reaction were found always to be depressed slightly. The ratio of $P_f/P_0$ remained essentially the same. The first half-dozen runs made in the clean, packed reaction vessel gave very heterogeneous results, but after the bulb became well coated with a deposit of silicon the results were quite reproducible.

From these experiments it is concluded that the decomposition of silicon tetraethyl is predominately homogeneous in nature. The secondary stages of this reaction involving mainly the decomposition of hydrocarbons seem to be slightly heterogeneous in character. It may well be that the lack of exact reproducibility manifested in the later stages of this reaction is due to the slight changes which take place on the surface of the bulb from run to run.

Nitric oxide has essentially the same effect in the packed as in the unpacked vessel, except that in the secondary stages the reaction appears to be inhibited to a slightly greater extent.

A series of runs were carried out to determine the effect of various reaction products, which proved to be negligible.

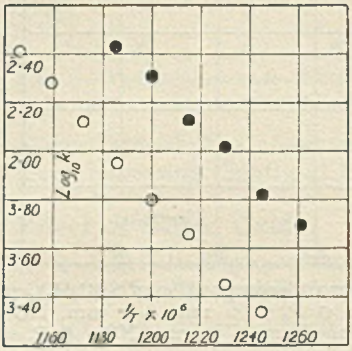

FIG. 6.—White circles, $Si(C_2H_5)_4$, $E_a = 51{,}000$ cal. Black circles, $Si(C_3H_7)_4$, $E_a = 46{,}000$ cal.

### 6. Energy of Activation.

A plot of the logarithm of the initial rate against the reciprocal of the absolute temperature (Fig. 6) gave a sensibly straight line. From data at eight different temperatures over a range of 80° C., the activation energy of $Si(C_2H_5)_4$, determined by the method of least squares, was 50,500 cal. Since this value is based upon data obtained over the initial stage of the decomposition, namely $Si(C_2H_5)_4 = Si + 4C_2H_5$, or $Si(C_2H_5)_4 = Si(C_2H_5)_3 + C_2H_5$, this activation energy should give some information as to the strength of the carbon-silicon bond.

## Silicon Tetrapropyl.

### 1. Nature of the Decomposition.

We might expect the decomposition of $Si(C_3H_7)_4$ to follow along the same lines as that of the ethyl compound. In general, this expectation is borne out. The procedure in studying this reaction was the same as that previously employed.

Silicon tetrapropyl decomposes to give a total pressure increase, on the average, of about 3·5 times that of the initial pressure. The ratio of the final to the initial pressure is less reproducible than that of silicon tetraethyl, and varies between 3·0 and 4·0. However, the same type curve as that for $Si(C_2H_5)_4$ (Fig. 1) is followed. Temperature changes appeared to have no effect. At all temperatures the reaction approached the end-point very slowly. For example, at 560° C.—within 10° of the highest temperature investigated—the end-point had not been reached after four and one-half hours.

Hence, we are again confronted with the problem of the best method for determining a rate constant which will give the correct order of the reaction. In some respects, the decomposition of $Si(C_3H_7)_4$ is analogous to that of propane (Hobbs and Hinshelwood [8]) where the great complexity of the secondary reactions made it advisable to base measurements upon the initial rate. Since $Si(C_3H_7)_4$ gives even more complex reactions we have decided to adopt the same procedure, as again we are mainly interested in the primary process.

## 2. Reaction Products.

Samples were withdrawn from the reaction vessel at various time intervals throughout the course of the reaction at 550° C., where the initial rate of reaction of $Si(C_3H_7)_4$ was approximately the same as that of $Si(C_2H_5)_4$ at 580° C. These results are presented graphically in Fig. 7.

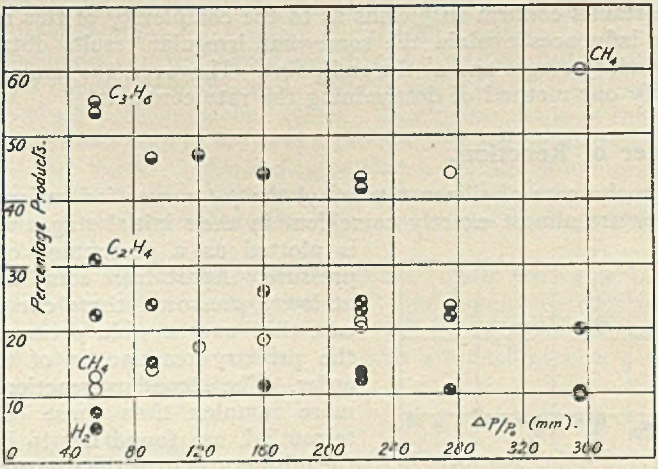

FIG. 7.—Showing the change in reaction products during the course of the decomposition of $Si(C_3H_7)_4$ at 550° C.
⊖—$C_3H_6$; ⊘—$C_2H_4$; ●—$H_2$; ⊙—$CH_4$.

By way of variation, the percentage of reaction products at various pressure differences rather than the various times are recorded in this case. By extrapolation to zero pressure it can be seen that the primary product is predominantly a higher olefine, most probably propylene, which suggests as the primary step

$$Si(C_3H_7)_4 = Si + 4C_3H_7,$$

$$\text{or} \quad Si(C_3H_7)_4 = Si(C_3H_7)_3 + C_3H_7 \text{ (slow)},$$
$$Si(C_3H_7)_3 = Si + 3C_3H_7 \text{ (fast)}.$$

The amount of hydrogen is about half that found in the case of $Si(C_2H_5)_4$. On the basis of the proposed primary processes, there is little reason for the amounts of hydrogen to differ appreciably, unless, in one case, some of the hydrogen atoms react in some manner other than a simple recombination process. Since the hydrogen concentration remains constant after the early stage of the reaction, and since the ethylene concentration remains sensibly unchanged until the end-point is approached, it may be inferred that the secondary reactions are

$$\begin{gathered} C_3H_7 = C_3H_6 + H, \\ 2H = H_2 \text{ (fast)}, \\ C_3H_6 + 2H = C_2H_4 + CH_4 \text{ (fast)}. \end{gathered}$$

Total pressure increases are affected to a greater extent by the same factors as discussed with the previous compound.

Before any end-point run had been made the only deposit in the reaction vessel was silicon, but afterwards carbon was also found, suggesting the reaction

$$C_2H_4 = CH_4 + C,$$

as found with the silicon tetraethyl. A further indication that the decomposition of $Si(C_3H_7)_4$ proceeds by a mechanism which is essentially the same as that of $Si(C_2H_5)_4$ is the fact that no saturated hydrocarbon other than methane could be found in the gaseous products. In all analyses the mean number of carbon atoms was 1·0.

The results confirm suspicions as to the complexity of this reaction. Surface influences explain the somewhat irregular results obtained in the secondary stages and at the end-point. However, the analyses seem to justify our method of determining the rate constant.

## 3. Order of Reaction.

As in the case of silicon tetraethyl the *p-t* curves for various initial pressures are almost exactly coincident in their initial stages when $\Delta p$ is plotted as a percentage of initial pressure. Apart from some deviation at lower pressures, these curves indicate that over a wide pressure range the primary reaction is of the first order. The secondary reactions, while more complex than those of silicon tetraethyl, are found not to influence the initial rates over the pressure range investigated.

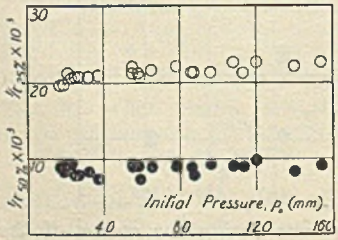

Fig. 8.—Variation of the reciprocal of percentage pressure increase with initial pressure at 530° C. for $Si(C_3H_7)_4$.

The curves in Fig. 8 show the reciprocals of a 25 and 50 per cent. pressure increase plotted as a function of the initial pressure. Even though there is a tendency for the rate to fall off at low initial pressures, the reaction is clearly of the first order over a wide pressure range. We conclude, then, from measurements based upon initial rates and times for a given fractional increase of the initial pressure that the decomposition of $Si(C_3H_7)_4$, like that of $Si(C_2H_5)_4$, is predominantly of the first order. Accidental compensation of error would be unlikely to lead to the same result by both methods.

## 4. Effect of Nitric Oxide.

As with the tetraethyl compound, small quantities of NO had no effect. With 25-35 mm. NO, however, the secondary processes were noticeably inhibited though the primary process was affected to only a very slight degree. The substantial effect on the total pressure increase with larger amounts of NO indicates that radicals have, in fact, been present during the reaction ; the absence of any marked inhibition in the initial rate shows that these radicals have not propagated chains with the primary reactants.

By the arguments previously used, the propyl radicals formed in the primary process disappear according to reactions of which the principal one is

$$C_3H_7 = C_3H_6 + H.$$

Here, however, only half the hydrogen atoms are removed by simple recombination, the other half reacting with the secondary products, probably in the manner

$$C_3H_6 + 2H = C_2H_4 + CH_4.$$

## 5. Surface Effects.

A new reaction vessel packed with uniform bits of pyrex tubing had a surface/volume ratio 10 times greater than that of the unpacked bulb. The first half-dozen or so runs gave an abnormally fast initial rate over the first two minutes after which they slowed down abruptly. With each subsequent run the initial rate became slower until finally reproducible *p-t* curves were obtained. The initial rates of these runs correspond to those in the unpacked vessel. Check runs made in the packed vessel after it had been in use over a three-month period showed that the rates had not varied. This indicates that a certain minimum coating of silicon on the walls is necessary for reproducibility, but that after a lower limit is attained subsequent layers of silicon have no effect upon the initial process.

With a new 250 c.c. unpacked bulb the results were essentially the same. The only exception was that the " conditioning period " necessary for reproducibility was much shorter.

These results seem to indicate that we are dealing with a reaction which borders on heterogeneity.

## 6. Activation Energy.

From the initial rates at six different temperatures (*cf.* Fig. 6) the activation energy was determined by the method of least squares. Its value was 46,000 cal., which is about 4,500 cal. less than that of the ethyl compound. One does not know, exactly, whether to attribute this difference to the negative influence of the additional $CH_3$ substituent which tends to weaken the Si—C bond, or to slight differences in the reaction mechanisms (*vide supra*).

Data available showed that the final gaseous decomposition products of silicon tetramethyl are mainly methane and hydrogen, carbon and silicon being deposited on the walls. No ethane was found. The amount of hydrogen formed is about 40 per cent., a somewhat higher value than that for the tetraethyl which itself is 50 per cent. higher than that of the propyl. Based on these facts, the probable mechanism that suggests itself for the methyl compound is

$$Si(CH_3)_4 = Si + 4CH_3,$$
$$\text{or}\quad Si(CH_3)_4 = Si(CH_3)_3 + CH_3 \text{ (fast)},$$

followed by

$$2CH_3 = C_2H_4 + 2H \text{ (practically complete)},$$
$$2H = H_2 \text{ (fast)},$$
$$C_2H_4 = CH_4 + C.$$

The published results for the activation energy (Helm and Mack [3]) is 79,000, but since this was determined for a range of 20-80 per cent. pressure change, it is by no means strictly comparable with the present results.

Table I gives a comparison between the results obtained in the kinetic studies on silicon tetraethyl and silicon tetrapropyl.

TABLE I.—COMPARISON BETWEEN $Si(C_2H_5)_4$ AND $Si(C_3H_7)_4$.

| T° C. | $Si(C_2H_5)_4$. | $Si(C_3H_7)_4$. | Ratio. $k_{Pr}/k_{Et}$. |
|---|---|---|---|
| | Approx. $k_1 \times 10^{-3}$ sec.$^{-1}$. | Approx. $k_1 \times 10^{-3}$ sec.$^{-1}$. | |
| 520 | — | 1·43 | — |
| 530 | 0·875 | 1·85 | 2·12 |
| 540 | 1·08 | 3·00 | 2·77 |
| 550 | 1·83 | 3·83 | 2·09 |
| 560 | 2·53 | 5·85 | 2·31 |
| 570 | 3·26 | 7·68 | 2·36 |
| 580 | 5·28 | — | — |
| 590 | 7·75 | — | — |
| 600 | 10·35 | — | — |

*Ratio of $P_fP_0$.*

| | $Si(C_2H_5)_4$. | $Si(C_3H_7)_4$. |
|---|---|---|
| From | 2—3 | 3—4 |
| Av. | 2·5 | 3·5 |

*Activation Energy.*

| $Si(C_2H_5)_4$. | $Si(C_3H_7)_4$. |
|---|---|
| 50,500 | 46,000 |

## Summary.

The thermal decomposition of silicon tetraethyl and silicon tetrapropyl is kinetically complex. By the criteria of initial rates, half-life periods and times for a given fractional pressure increase, the primary process, in both cases, is found to be predominantly of the first order. At lower initial pressures the order increases slightly.

Both reactions are homogeneous over the primary stage but show some tendency toward heterogeneity in the secondary processes, this effect being greater in the case of the propyl compound.

Small amounts of NO have no effect. Large quantities of NO inhibit the primary process of both reactions only slightly, indicating that radicals

are formed initially but that long chains are not propagated with the primary reactant. The secondary processes of both reactions are markedly inhibited by large amounts of NO. Chemical analyses made on the gaseous products over the entire decomposition range together with the kinetic data indicate that the predominant reaction mechanisms are :

Silicon Tetraethyl

Primary Process $Si(C_2H_5)_4 = Si + 4C_2H_5$,
or, $Si(C_2H_5)_4 = Si(C_2H_5)_3 + C_2H_5$ (slow),
$Si(C_2H_5)_3 = Si + 3C_2H_5$ (fast).

Secondary Process $C_2H_5 = C_2H_4 + H$,
$2H = H_2$ (fast),
$C_2H_4 = CH_4 + C$ (slow).

Silicon Tetrapropyl

Primary Process $Si(C_3H_7)_4 = Si + 4C_3H_7$,
or, $Si(C_3H_7)_4 = Si(C_3H_7)_3 + C_3H_7$ (slow),
$Si(C_3H_7)_3 = Si + 3C_3H_7$ (fast).

Secondary Process $C_3H_7 = C_3H_6 + H$,
$2H = H_2$ (fast),
$C_3H_6 + 2H = C_2H_4 + CH_4$,
$C_2H_4 = CH_4 + C$ (slow).

The author wishes to express his thanks to the Lalor Foundation, whose grant of a Fellowship has made possible these investigations.

The author is also deeply grateful to Professor C. N. Hinshelwood for his continual guidance, interest and advice throughout the course of this research.

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# ON AN ORTHORHOMBIC CRYSTALLINE MODIFICATION OF DIPHENYL OCTATETRAENE.

By K. S. Krishnan, S. L. Chorghade and T. S. Ananthapadmanabhan.

*Received 4th September*, 1940.

The diphenyl polyenes, having the general formula

$$C_6H_5—(CH=CH)_n—C_6H_5,$$

with alternate single and double bonds in the central chain, are an interesting class of compounds from many different points of view. The crystal structures of several of them have been studied by X-ray methods by Hengstenberg and Kuhn,[1] who find that while the earlier members of the series, namely those for which $n = 1$ to 4, crystallise in the monoclinic system, the higher members investigated by them, namely those for which $n = 5$ to 7, crystallise in the orthorhombic system. Recently while crystallising some diphenyl octatetraene (the compound with $n = 4$) from its solution in ethyl acetate, there appeared in the crop, along with the many flaky crystals, which were monoclinic and had the axial dimensions given by Hengstenberg and Kuhn, also several thick

[1] *Z. Kristallog. A*, 1930, 75, 301.

plates, which were found to be orthorhombic and to belong to the same series in which the higher polyenes, with $n$ greater than 4, crystallise. In the present paper * is given an account of some goniometric and X-ray studies on this orthorhombic modification of diphenyl octatetraene.

## Preparation of Diphenyl Octatetraene and its Identification.

The compound was prepared by the method described by Kuhn and Winterstein,[2] namely by the condensation of cinnamaldehyde with succinic acid in the presence of lead monoxide, and purified by repeated crystallisations. The substance is golden yellow and can be crystallised from solutions in any of the usual organic solvents. The crop of crystals obtained from a solution in ethyl acetate contains, as we mentioned just now, both the monoclinic (usually large and flaky) and the orthorhombic (usually stout and well-developed) varieties. The crystals obtained from a solution in benzene, or in ethyl acetate to which has been added some benzene, are predominantly of the monoclinic variety, whereas those obtained from a solution in chloroform are predominantly of the orthorhombic variety. The chemical identity of the two types of crystals is verified by the observation that starting from either type of crystals one can obtain, by dissolving in suitable solvents and recrystallising, both the types. The monoclinic crystals had a melting-point of 227° C., which agrees well with the value 232° C. given by Kuhn and Winterstein. The orthorhombic crystals too had practically the same melting-point, namely 226° C.

Both the varieties answered to the following chemical tests given by Kuhn and Winterstein. When melted with *s*-trinitrobenzene, they gave a reddish brown solution, and with cold concentrated sulphuric acid they gave a violet colour, which after some time deepened to dark pink. Further a solution in chloroform was found to decolourise a dilute solution of bromine in chloroform, as should be expected from the presence of double bonds in the molecule.

Finally, an X-ray analysis of the flaky crystals, by the rotation method, gave the following dimensions for the unit cell :

$$a = 6{\cdot}24,\ b = 7{\cdot}42,\ c = 16{\cdot}09\ \text{A},\ \beta \sim 90^\circ,$$

which agree well with the dimensions

$$a = 6{\cdot}25,\ b = 7{\cdot}44,\ c = 16{\cdot}03\ \text{A},\ \beta \sim 90^\circ$$

obtained by Hengstenberg and Kuhn. The cell contains 2 molecules of $C_6H_5$—$(CH{=}CH)_4$—$C_6H_5$.

## Orthorhombic Modification : Goniometric Measurements.

The stout, well-developed crystals of diphenyl octatetraene, were measured goniometrically, and were found to belong to the orthorhombic bipyramidal class, having the axial elements

$$a : b : c = 1{\cdot}319 : 1 : 2{\cdot}615.$$

The crystals were thick plates parallel to {001}, with the side faces {010}, {012} and {111} also well-developed. The measured angles between the various faces are given in Table I, along with the angles calculated from the above axial ratios for comparison.

TABLE I.

| | Measured. | Calculated. |
|---|---|---|
| (111) : (001) | 73° 3′ | — |
| (111) : (010) | 40 20 | — |
| (111) : $(1\bar{1}1)$ | 80 40 | 80° 41′ |
| (111) : $(\bar{1}11)$ | 70 41 | 70 36 |
| (111) : $(11\bar{1})$ | 33 54 | 33 53 |
| (012) : (001) | 52 29 | 52 36 |

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* A preliminary note appeared in *Nature*, 1940, 146, 333.

[2] *Helv. Chim. Acta*, 1928, 11, 87.

## Orthorhombic Modification: X-ray Studies.

Rotation photographs taken about the *a*, *b*, and *c* axes gave the following dimensions for the unit cell :

$$a = 9{\cdot}95,\ b = 7{\cdot}55,\ c = 19{\cdot}75\ \text{A},$$

which bear the ratios

$$a : b : c = 1{\cdot}318 : 1 : 2{\cdot}616,$$

which are almost the same as the goniometric ratios. The density of the crystal, as measured by the flotation method, was 1·140 g./c.c., and it corresponds to 4 (3·95) molecules of $C_6H_5$—$(CH{=}CH)_4$—$C_6H_5$ in the unit cell.

## Comparison of the Unit Cell Dimensions with those of the Higher Polyenes.

The above cell dimensions fit well with the dimensions of the unit cells of the higher members in the series, as will be seen from the following table. The number of molecules in the unit cell is 4 in all the crystals. Thus diphenyl octatetraene is dimorphous, and one of the modifications belongs to the monoclinic system, in which the earlier members of the diphenyl polyenes crystallise, and the other to the orthorhombic series to which the higher members belong. We are now studying the crystal structures of the adjacent members in the polyene series, namely those for which $n = 3$ and 5 respectively, to find whether they too exhibit similar dimorphism and appear in both the monoclinic and the orthorhombic modifications.

TABLE II.

| *n*. | *a* (A). | *b* (A). | *c* (A). |
|---|---|---|---|
| 4 | 9·95 | 7·55 | 19·75 |
| 5 | 10·25 | 7·66 | 21·2 |
| 6 | 10·20 | 7·60 | 23·58 |
| 7 | 10·2 | 7·57 | 25·95 |

## Summary.

The crystal structures of the diphenyl polyenes having the general formula $C_6H_5$—$(CH{=}CH)_n$—$C_6H_5$ have been studied before, by Hengstenberg and Kuhn, and it is known that while the earlier members in the series with $n = 1$ to 4 crystallise in the monoclinic system, the higher members studied by them crystallise in the orthorhombic system. In the present paper it is shown that diphenyl octatetraene (the compound with $n = 4$) is dimorphous ; it crystallises not only in the monoclinic system, as the earlier members do, but also in the orthorhombic system in the same series as the higher members.

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*Cultivation of Science, Calcutta.*

# THE CALCULATION OF SURFACE TENSION FROM INTERMOLECULAR FORCES.

By J. E. Lennard-Jones and J. Corner.

*Received 26th August*, 1940.

## 1. Introduction.

Although this subject has been discussed many times in the past, it has not yet been treated, so far as we know, in terms of modern theories of liquid structure and intermolecular forces. We must except the very revealing work of Fowler,[1, 2] who discussed the surface tension of liquids near the critical point. He obtained a theoretical formula for the parachor and showed that it is indeed a constant near the critical point, the numerical agreement being as good as can be expected from molecules which are rigid spheres with an $r^{-6}$ attractive potential. The development of Mayer's theory[3] and the experimental results of Maass and his collaborators[4] have made some of Fowler's assumptions about the critical point seem less obvious, but this affects his argument only within a few degrees of the critical point; for some rather uncertain range of lower temperatures the theory proves the constancy of the parachor. It does not, however, apply to temperatures in the neighbourhood of the melting-point or the boiling-point. Fowler[2] did indeed calculate the parachor at low temperatures, without proving that it is independent of the temperature in this range. He found values much greater than those calculated near the critical point with the same intermolecular fields. This was because the free energy per unit area (or surface tension) $\sigma$ was assumed to be approximately equal to the surface energy per unit area $U_s$, and it was the latter which was calculated and used for $\sigma$. Actually, $U_s$ proves to be about three times the value of $\sigma$ near the melting-point.*

There has been much confusion between surface energy and surface free energy. It has been clearly pointed out by Fowler[1] that the work done by the molecular forces when a column of liquid is broken and the two halves moved to infinite separation in a reversible isothermal process, is equal to the decrease in the Gibbs free energy of the system, and so is related to $\sigma$. The assumption that this work is the decrease of the total energy of the system invalidates the work of Bradley[5] and Margenau.[6]

The probability of finding a molecular centre in a volume $d\tau$ at a distance $r$ from the centre of any molecule is usually written as

$$4\pi r^2 \rho g(r) d\tau$$

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[1] R. H. Fowler, *Proc. Roy. Soc.*, *A*, 1937, **159**, 229.

[2] R. H. Fowler, *Physica*, 1938, **5**, 39.

[3] J. E. Mayer and S. F. Harrison, *J. Chem. Physics*, 1938, **6**, 87.

[4] O. Maass and A. L. Geddes, *Phil. Trans. Roy. Soc.*, *A*, 1937, **236**, 303.

* We are indebted to Professor R. H. Fowler for confirming this correction.

[5] R. S. Bradley, *Phil. Mag.*, 1931, **11**, 846.

[6] H. Margenau, *Physic. Rev.*, 1931, **38**, 365.

where $\rho$ is the average density and $g(r)$ is the neighbour distribution function. For a very dilute gas,

$$g(r) = e^{-E(r)/kT} \quad . \quad . \quad . \quad . \quad (1)$$

where $E(r)$ is the potential energy of a pair of molecules at distance $r$ apart. It is now accepted that in a liquid $g(r)$ deviates widely from this value, especially for small $r$; thus integrations of interaction energies between the molecules of a liquid must use a $g(r)$ which bears a resemblance to that of a solid. The assumption (1) can be used to find the surface tension of a dilute gas, but not a liquid. This improper application was made by Margenau.[6] The more crude approximation that $g(r) = 1$ for $r$ greater than the molecular diameter, with $g(r)$ zero for smaller $r$, was used in the classical Rayleigh-Laplace calculations.[7] This lead was followed by Edser,[8] Bradley [5] and Wheeler.[9]

Several workers have used the model of rigid spheres, diameter $\delta$, with an attractive potential varying as an inverse power of the distance, *viz.* $-Ar^{-n}$, where $r$ is the distance between the centres of the molecules. Fowler [1] and Margenau [6] took $n = 6$, which is suggested by quantum mechanics, and $A$ and $\delta$ constant; Edser [8] took $n = 7$, with $\delta$ constant, but $A$ varying with the temperature; Wheeler [9] followed Edser's work, but kept $A$ constant and allowed $\delta$ to vary with temperature, arriving at the conclusion that $n$ must be about 9 or 10.

We use the intermolecular potential

$$E(r) = 12\phi_0\left\{\frac{1}{12}\left(\frac{r_0}{r}\right)^{12} - \frac{1}{6}\left(\frac{r_0}{r}\right)^{6}\right\} \quad . \quad . \quad . \quad (2)$$

where $\phi_0$ and $r_0$ are constants of energy and length, characteristic of the molecule, and $r$ is the distance between the molecular centres. This has proved to be very successful in accounting for the second virial coefficients of gases with quasi-spherical molecules, and many other properties of liquids and solids.[10] We use the same ideas of the structure of a liquid as in previous papers from this laboratory,[11–14] and as in these papers we consider only cases in which the molecules are effectively spherical when in motion in the liquid state. In the present note we discuss the formal relationships between surface tension and other properties which can be deduced from these assumptions. In a later paper we hope to give the results of numerical calculations of surface tensions and surface energies by these methods.

## 2. General Relations between Surface Tension and Intermolecular Forces.

We will consider a reversible process at constant temperature and pressure in which the surface is increased by one unit; the mechanical work required to perform this process is the increase in the Gibbs free energy $G$ of the system. The changes in $PV$ are, however, very small,

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[7] Lord Rayleigh, *Phil. Mag.*, 1890, **30**, 285, 456.

[8] E. Edser, *Fourth Report on Colloid Chemistry*, H.M.S.O., 1922, p. 40.

[9] T. S. Wheeler, *Ind. J. Physics*, 1934, **3**, 521; *Proc. Ind. Acad. Sci., A*, 1934, **1**, 105.

[10] J. E. Lennard-Jones, *Physica*, 1937, **4**, 941.

[11] J. E. Lennard-Jones, and A. F. Devonshire, *Proc. Roy. Soc., A*, 1937, **163**, 53.

[12] *Ibid.*, 1938, **165**, 1.

[13] *Ibid.*, 1939, **169**, 317.

[14] *Ibid.*, 1939, **170**, 464.

so that in these calculations we need only consider changes in the Helmholtz free energy $A$.

We consider $N$ molecules in a volume $V$, and for the present we neglect the effect of the boundary. The intermolecular potential is (2). We write

$$V_0 = NV_0^* = Nr_0^3 2^{-1/2} \quad . \quad . \quad . \quad (3)$$

With this notation the partition function of the liquid is $F(T)$, where

$$\log F = -\frac{\Phi_0}{kT} + \frac{3N}{2}\log\left(\frac{2\pi mkT}{h^2}\right) + N\log V_f^* + N\alpha \quad . \quad (4)$$

This partition function is relative to an energy-zero where all the molecules are infinitely separated; $\Phi_0$ is the potential energy of the molecules when arranged at their mean positions in a face-centred cubic lattice of infinite extent containing $N$ molecules per volume $V$, so that

$$\Phi_0 = 12N\phi_0\left\{0{\cdot}5\left(\frac{V_0}{V}\right)^4 - 1{\cdot}2\left(\frac{V_0}{V}\right)^2\right\} \quad . \quad . \quad (5)$$

$v_f^*$ is the free volume of an atom when all the others are fixed in their mean positions. The sharing of free volume is taken into account by the term $\alpha$, whose extreme values are 0 (for no sharing) and 1 (complete sharing). This partition function has been discussed in previous papers,[11–13] and formulæ for $v^*$ and $\alpha$ have been given. These will not be needed in the present paper. The Helmholtz free energy

$$\begin{aligned} A &= -kT\log F \\ &= \Phi_0 - \frac{3NkT}{2}\log\left(\frac{2\pi mkT}{h^2}\right) - NkT\log V_f^* - N\alpha kT \quad . \quad (6) \end{aligned}$$

Let $N_s$ be the average number of molecules on unit area of the surface. A molecule at the surface will have a bigger free volume than a molecule in the body of the liquid, for the former will not be tightly bound in a direction normal to the surface. Let the free volume of a surface molecule be denoted by $V_s^*$. It is plausible to suppose that the possibility of sharing its free volume with the other molecules will not be greatly altered.

Now suppose that the volume $V$, containing $N$ molecules, is made to take the shape of a long column of cross-section 1/2. Let the surface of this be named $S$. The increase in the free energy will be denoted by $A_0$, which must be added to the right side of (6). $A_0$ will, of course, be a function of the temperature, as it will be the sum of the changes in the potential energy and the free volume terms, but as it will cancel from our equations we need not calculate its value. We now break the column at its central cross-section and move the two halves to an infinite distance apart in an isothermal reversible process. With the same energy zero, the free energy is now

$$\begin{aligned} A_2 = A_0 + \Psi_0 - \tfrac{3}{2}NkT\log\left(\frac{2\pi mkT}{h^2}\right) - N\alpha kT \\ - (N - N_s)kT\log V_f^* - N_s kT\log V_s^* \quad (7) \end{aligned}$$

instead of, as previously,

$$A_1 = A_0 + \Phi_0 - \tfrac{3}{2}NkT\log\left(\frac{2\pi mkT}{h^2}\right) - N\alpha kT - NkT\log V_f^* \quad (8)$$

$\Psi_0$ is the potential energy of the $N$ molecules in their equilibrium positions in the infinitely separated halves of the column, without any correction for the effect of the surfaces $S$. This correction is, of course, included in $A_0$. The point of this formulation is that $\Psi_0$ is just the energy of the $N$ molecules in a column of volume $V$ and unit cross-section, immersed in a semi-infinite liquid of the same constitution with a plane face, at which the column terminates. This energy can be calculated by a lattice summation.

In this process of breaking the column we have created an extra unit of surface, so that the increase in the free energy of the system is

$$\sigma = A_2 - A_1 = \Psi_0 - \Phi_0 + N_s kT \log (V_f^*/V_s^*) \quad . \quad . \quad (9)$$

$V_s^*$ and $V_f^*$ vary only slowly with the temperature, and the former is the larger, so that $\sigma$ decreases with increase of temperature. If we neglect the temperature variation of the ratio of the free volumes, and use the fact that $\Psi_0 - \Phi_0$ and $N_s$ are proportional to the surface density of atoms, and so to $V^{-2/3}$, we obtain the relation

$$\sigma V^{2/3} = \kappa(T_0 - T)$$

where $\kappa$ and $T_0$ are constants. This is just Eotvos' law,[15] which is known to hold at low temperatures; $\kappa$ is often about 2·1 ergs/degree, and $T_0 \simeq T_c$. By taking a plausible approximation for the change in the free volume, Madelung[16] obtained $\kappa$ near the observed value. Born and Courant[17] replaced the liquid by an elastic continuum, as in Debye's theory of specific heats, and obtained a formula for $\kappa$ which agreed with experiment to within a few per cent. In a later paper we will present the results of a calculation of $\kappa$ and $T_0$ by the methods of Lennard-Jones and Devonshire.[11]

When the vapour density is not negligible compared with the liquid density, it is known that Eotvos' law must be replaced by the modification due to Katayama[18]

$$\sigma\left(\frac{M}{\rho_l - \rho_v}\right)^{2/3} = \kappa(T_c - T) \quad . \quad . \quad . \quad (11)$$

where $\rho_l$ and $\rho_v$ are the liquid and vapour densities respectively, and $M$ is the chemical molecular weight. The parachor $[P]$ is defined as

$$[P] = \frac{M\sigma^{1/4}}{\rho_l - \rho_v} \quad . \quad . \quad . \quad . \quad (12)$$

Any model of a liquid which gives (11) and the density law

$$\rho_l - \rho_v = \rho_0\left\{1 - \frac{T}{T_c}\right\}^{0\cdot3} \quad . \quad . \quad . \quad (13)$$

where $\rho_0$ is a constant, will give a constant parachor. This can be seen by replacing $\rho_l - \rho_v$ and $\sigma$ by their expressions as functions of $T_c - T$. The theory of melting proposed by Lennard-Jones and Devonshire[13] gives a density variation approximating to (13).

In passing we may point out that a comparison of the parachors of two liquids at low temperatures ($\rho_v \ll \rho_l$) is a comparison of their

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[15] Eotvos, *Wied. Ann.*, 1886, **27**, 456.
[16] E. Madelung, *Physik. Z.*, 1913, **14**, 729.
[17] M. Born and R. Courant, *ibid.*, 731.
[18] M. Katayama, *Tohoku Univ. Sci. Rep.*, 1916, **4**, 373.

molar volumes at equal *non-zero* surface tensions. This is not the same as a comparison of their critical volumes, as Sugden[19] suggests. Since $[P]$ has the dimensions of $(\text{length})^{5/2}\,(\text{energy})^{1/4}$, a relation of the type

$$[P]V_c^{-5/6}T_c^{-1/4} = const. \quad . \quad . \quad . \quad (14)$$

is to be expected rather than

$$[P]V_c^{-1} = const. \quad . \quad . \quad . \quad . \quad (15)$$

as proposed by Sugden, or than a relation between $[P]$ and $T_c$, as suggested by Lewis.[20] Table I shows that the relation (14) is actually obeyed by a series of gases whose molecules may be regarded as spherical, whereas (15) is not. We have restricted our attention to gases whose force-constants are known, so that we might demonstrate the further relation

TABLE I.

THE PARACHOR IN TERMS OF PHYSICAL CONSTANTS.*

| Substance. | $[P]$. | $[P]V_c^{-1}$. | $[P]V_c^{-5/6}T_c^{-1/4}$. | $[P]r_0^{-5/2}\phi_0^{-1/4}$. |
|---|---|---|---|---|
| A | 54 | 0·718 | 0·421 | 5·26 × 10²³ |
| Ne | 25 | 0·600 | 0·432 | 5·69 |
| $N_2$ | 60·4 | 0·671 | 0·424 | 5·24 |
| CO | 61·6 | 0·662 | 0·415 | 5·12 |
| $CH_4$ | 73·2 | 0·742 | 0·429 | 5·31 |
| Average . . . . . | | 0·679 | 0·424 | 5·32 × 10²³ |
| Root mean square deviation/average . . . . | | 7·2 % | 1·4 % | 3·6 % |

* $[P]$ from Sudgen[19]; $\phi_0$ and $r_0$ for A and Ne from Fowler,[21] for CO and $CH_4$ from Corner,[22] but now taking $\phi_0$ from $kT_c = 1{\cdot}28\ \phi_0$; for $N_2$ from Corner[23]; other data from *International Critical Tables.*

$$[P]\phi_0^{-1/4}r_0^{-5/2} = const. \quad . \quad . \quad . \quad . \quad (16)$$

which follows from the method of dimensions. Here $\phi_0$ and $r_0$ are the constants of the intermolecular field, defined by (2), and have the dimensions of energy and length respectively. This relation might, in fact, be used to deduce approximate values of $r_0$, when $\phi_0$ is known from other methods.

Equation (14) can be applied to xenon,[24] for which $V_c = 114$ c.c./mole, and $T_c = 289{\cdot}9°$ K., giving $[P] = 90{\cdot}6$. This is in excellent agreement with Sugden's prediction[19] of 91. Sugden also estimated that $[P]$ for krypton would be about 68; actually[25] $T_c = 209{\cdot}4°$ K. and $V_c = 92{\cdot}1$ c.c./mole, so that according to (14) $[P]$ should be 69·6.

Helium and hydrogen have been omitted from our Table I because

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[19] S. Sugden, *The Parachor and Valency* (London), 1930.

[20] D. T. Lewis, *J. Chem. Soc.*, 1938, 261.

[21] R. H. Fowler, *Statistical Mechanics*, 1936, Cambridge, p. 306.

[22] J. Corner, *Trans. Faraday Soc.*, 1939, **35**, 711.

[23] J. Corner, *ibid.*, 1940, **36**, 780.

[24] H. S. Patterson, R. S. Cripps and R. Whytlaw-Gray, *Proc. Roy. Soc.*, 1912, **86**, 579.

[25] E. Mathias, C. A. Crommelin and J. J. Meihuizen, *Compt. Rend.*, 1937, **204**, 630.

quantum effects must be important here. Neon should perhaps be omitted for the same reason. The average results are then

$$[P] = 0{\cdot}422 V_c^{5/6}\, T^{1/4} \quad . \quad . \quad . \quad . \quad (17)$$

$$[P] = 5{\cdot}23 \times 10^{23} \phi_0^{1/4}\, r_0^{5/2} \quad . \quad . \quad . \quad (18)$$

Ferguson and Kennedy [26] have derived the empirical formula

$$[P] = 0{\cdot}324 T_c^{1/4} V_c^{7/8} \quad . \quad . \quad . \quad . \quad (19)$$

from data for over twenty organic substances. Many of these have such unsymmetrical molecules that hindrance to rotation must play an important part in the properties of their liquids. Nevertheless, the formula

$$[P] = 0{\cdot}410 V_c^{5/4} T_c^{1/4} \quad . \quad . \quad . \quad . \quad (20)$$

gives slightly better agreement than (19), and both are better than

$$[P] = 0{\cdot}768 V_c \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The numerical constants were found by least squares. The root-mean-square error of formulæ (19), (20) and (21) are respectively 6·5, 4·9 and 10·9; the average parachor of these substances is about 200.

The additive nature of the parachor has been found of great value to the chemist. It is not obvious why this function of the intermolecular forces, $\phi_0^{1/4}\, r_0^{5/2}$, should be additive when more complicated molecules are built up. If this involved only the attractive term one might be able to relate it to the numbers of electrons in the molecules, using such general relations as the Slater-Kirkwood formula. But the combination $\phi_0^{1/4}\, r_0^{5/2}$ also contains the constant of the repulsive forces, and there are no general rules for these.[27] From its interpretation as a collision volume, one would expect $r_0^3$ to be approximately additive, and this may be the reason for the apparent additivity of $\phi_0^{1/4}\, r_0^{5/2}$.

The surface energy per unit area

$$U_s = \sigma - T\frac{\partial\sigma}{\partial T} = \Psi_0 - \Phi_0 - N_s\left\{\frac{kT^2}{V_f^*}\frac{\partial V_f^*}{\partial T} - \frac{kT^2}{V_s^*}\frac{\partial V_s^*}{\partial T}\right\} \quad . \quad (22)$$

Now $\dfrac{kT^2}{V_f^*}\dfrac{\partial V_f^*}{\partial T}$ is the part of the potential energy of a molecule due to its motion about its equilibrium position. It is, for example, $3kT/2$ when the motion is like that of a harmonic oscillator. It will be nearly the same for a surface molecule as for one in the interior of the liquid, so that we may write

$$U_s \simeq \Psi_0 - \Phi_0 \quad . \quad . \quad . \quad . \quad (23)$$

Hence for the law of force (2) we must have

$$U_s = V^{-2/3}\phi_0 f(V_0/V) \quad . \quad . \quad . \quad . \quad (24)$$

But by Eotvos' law, $U_s V^{2/3}$ is independent of the temperature, at any rate at low temperatures, so that $f(V_0/V)$ should also be independent of the temperature over a considerable range of low temperatures. This can readily be understood. For $f$ will be of roughly the same form as the lattice energy of a crystal. Thus for a face-centred cubic crystal we have for $f$ a function of the form

$$1{\cdot}2\left(\frac{V_0}{V}\right)^2 - 0{\cdot}5\left(\frac{V_0}{V}\right)^4.$$

This varies only slowly with the volume near the usual liquid volumes of about $V_0$.

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[26] A. Ferguson and S. J. Kennedy, *Trans. Faraday Soc.*, 1936, **32**, 1474.

[27] H. London, *ibid.*, 1937, **33**, 8.

*Note added in Proof.*—Let $\mu = \sigma V^{2/3}$. Campbell and Eley [28] have shown that $T\frac{\partial \mu}{\partial T}$ is proportional to $\mu - T\frac{\partial \mu}{\partial T}$, for 40 substances at 25° C. Not all these obey Eotvos' law at this temperature; nevertheless the data is represented just as well by the relation, $T_c\frac{\partial \mu}{\partial T}$ proportional to $\mu - T\frac{\partial \mu}{\partial T}$, which follows from Eotvos' law on approximating to $T_0$ by $T_c$.

## Summary.

A discussion is given of the surface tension of liquids in terms of intermolecular forces. It is shown that certain empirical laws, which have been used extensively in the past, have a certain theoretical basis and can be deduced under certain conditions from intermolecular forces. There is a discussion of the parachor and some of its properties and a formula is given for it in terms of the constants of intermolecular fields.

We are indebted to Professor Allan Ferguson for a discussion of these matters. One of the authors is indebted to the Goldsmiths' Company for the award of a Senior Studentship.

*The University Chemical Laboratory,*
*Cambridge.*

[28] Campbell and D. D. Eley, *Trans. Faraday Soc.*, 1940, **36**, 854.

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# THE MOLECULAR WEIGHTS OF RUBBER AND RELATED MATERIALS.

## I. EXPERIMENTAL METHODS.

By G. Gee.

*Received 25th September*, 1940.

The molecular weight of a high polymeric material may be measured by three types of method, involving (*a*) the use of an ultracentrifuge, (*b*) the measurement of the osmotic pressure of a solution, or some thermodynamically related quantity, and (*c*) the application of Staudinger's well-known equation to calculate the molecular weight from the viscosity of a dilute solution. The difficulty and expense of erecting an ultracentrifuge precludes its general use, and our attention has been confined to the two remaining methods. In this paper we describe the various forms of apparatus employed and discuss the interpretation of the experimental results. Application of these methods is considered in following papers.

### (1) Osmotic Methods.

### (*a*) A New Form of Osmometer.

Various forms of osmometer have been described: [1] the one employed in this work is shown in Fig. 1. The cells which contain the solvent and solution are turned out of two substantial brass cylinders A, and are

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[1] See *inter alia* (*a*) Carter and Record, *J.C.S.*, 1939, 660; (*b*) Schulz, *Z. physik. Chem.* (*A*), 1936, **176**, 317; (*c*) Meyer, Wolff and Boissonas, *Helv. chim. acta*, 1940, **23**, 430.

connected to glass tubes by means of copper-glass seals B which are soldered into the brass blocks. These seals are tested before use and rejected unless vacuum-tight. The lower cell communicates with a fine capillary tube (*ca.* ½ mm. diam.) which is bent into a U-shape as shown. The volume of this cell must be kept as small as possible in order to minimise the fluctuations of the liquid level in the capillary consequent upon temperature variations. Most of the volume of the cell is therefore filled by a perforated brass plate C, the upper surface of which is slightly domed and covered by a piece of fine copper gauze, soldered round the edges ; the object of this plate is to support the membrane D. The upper cell terminates in a glass tube E, of bore approximately 2 mm. greater than the external diameter of the capillary tube inserted in it. This capillary is of the same bore as that attached to the lower cell, so as to permit a direct reading of the pressure head across the cell without a capillarity correction. The hydrostatic pressure can be adjusted by moving the capillary up or down in the tube E. The inner faces of the brass cylinders are carefully polished flat and the two cells firmly clamped together by a ring of eight 0 BA screws : no trouble has ever been experienced from leakage between these faces. The outer ring F fits tightly around the lower cell and enables the face of this cell to be completely flooded with solvent when assembling the osmometer. The membranes used were obtained from Membranfilter-Ges. m.b. H., Gottingen, and are the grade known as " Ultracellafilter, feinst." They were obtained wet with water and before use are washed with alcohol and then with the solvent to be employed. The cells are cleaned by steaming and then washing with acetone, followed by the solvent to be used. The plate C is heated in a little boiling solvent to expel air entrapped by the gauze. In filling the osmometer the lower cell is flooded with solvent, any air bubbles removed from the capillary, and the plate and membrane placed successively in position. The upper cell is then lowered into place and clamped down before the whole assembly is suspended by a suitable cradle in a water thermostat. The upper cell is filled and emptied by means of a tube whose length is adjusted so that its tip just touches the membrane. In changing from one solution to another it is found sufficient to suck out the old solution, wash with two changes of the new solution, and fill. Washing is carried out by sucking the solution up into the filling tube and allowing it to flow back again : this is usually repeated three times. The advantage of this arrangement is that it is unnecessary to dismantle the osmometer to change solutions. If the membrane were perfectly semipermeable the solvent in the lower cell would remain unchanged indefinitely. In practice the upper cell is filled with solvent after each osmotic pressure measurement to check the constancy of the zero and a correction applied for the small pressures which are found. If the solution admitted to the upper cell contains a diffusible component, some of this will find its way into the lower cell from which it can only be removed again either by dismantling the osmometer or by prolonged washing of the upper cell with repeated changes of solvent : the latter is usually the simpler method. In this way the life of an osmometer, once assembled, is very long.

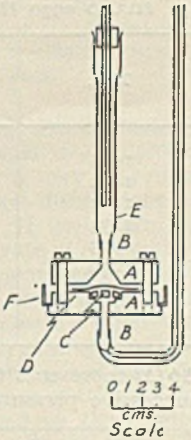

FIG. 1.—Construction of osmometer.

Two methods are available for estimating the equilibrium osmotic pressure : (*a*) the static method, in which osmosis is allowed to continue until equilibrium is attained, and (*b*) the dynamic method, in which the rate of osmosis is measured as a function of the pressure head across the osmometer and the osmotic pressure obtained by interpolating to zero rate of osmosis. Both these methods are readily applied to the present osmometer. If the pressure head $p$ is observed as a function of time $t$ the rate of osmosis is measured by $dp/dt$, and an extrapolation of the linear plot of $dp/dt - p$ enables the osmotic pressure to be estimated within about 5-8 hours of introducing the solution. If the solution is allowed to remain in the osmometer overnight an equilibrium value is also obtained, which in general agrees well with the dynamic value. Experience leads us to prefer the dynamic value when a discrepancy is found, since this can generally be attributed to instability of the solution, to very slow diffusion of solute through the membrane, or to slight contamination of the solution. Whichever method is employed accurate temperature control is essential, but this is doubly necessary with the dynamic method in order to prevent apparent rates of osmosis being complicated by thermal oscillation of the level in the lower cell. The thermostat employed in the present work is heated by a radiator lamp and controlled by a large spiral mercury-toluene thermoregulator and "Sunvic" relay. By careful arrangement of the stirrer, heater and regulator the temperature fluctuation at 25° C. has been reduced to ± 0·003° C. without any lagging.

The results of a typical experiment are set out in detail below :—

TABLE I.—OSMOTIC PRESSURE OF GEL RUBBER IN BENZENE + 15 % METHANOL. CONCENTRATION OF SOLUTION = 1·21 G./100 C.C. SOLUTION. OSMOMETER FILLED 0930 HR.

| Time. | Osmotic Pressure $p$ (mm. Solution). | $\Delta p/\Delta t$ (mm. Solution) hrs. | $\bar{p}$ (mm. Solution). |
|---|---|---|---|
| 1003 | $8{\cdot}6_{2}$ | — | — |
| 1032 | $10{\cdot}9_{2}$ | $4{\cdot}7_{5}$ | $9{\cdot}7_{7}$ |
| 1104 | $12{\cdot}6_{1}$ | $3{\cdot}2$ | $11{\cdot}7_{7}$ |
| 1134 | $13{\cdot}7_{4}$ | $2{\cdot}2_{5}$ | $13{\cdot}1_{7}$ |
| 1205 | $14{\cdot}4_{0}$ | $1{\cdot}3$ | $14{\cdot}0_{7}$ |
| 1249 | $15{\cdot}3_{0}$ | $1{\cdot}2$ | $14{\cdot}8_{5}$ |
| 1405 | $15{\cdot}8_{5}$ | $0{\cdot}4_{5}$ | $15{\cdot}5_{7}$ |
| 1552 | $16{\cdot}4_{6}$ | $0{\cdot}3_{5}$ | $16{\cdot}1_{5}$ |

$\Delta p/\Delta t$ represents the mean rate of osmosis over the interval between two successive pressure readings ; $\bar{p}$ is the mean of these two pressures. A plot of $\Delta p/\Delta t$ against $\bar{p}$ is given in Fig. 2, and extrapolation to zero rate of osmosis gives for the osmotic pressure a value of 16·4 mm. solution. This is to be compared with the static value (after standing overnight) of 16·8 mm. As already explained, the former value is taken to be correct. The normal experimental error is estimated to be not more than ± 0·5 mm.

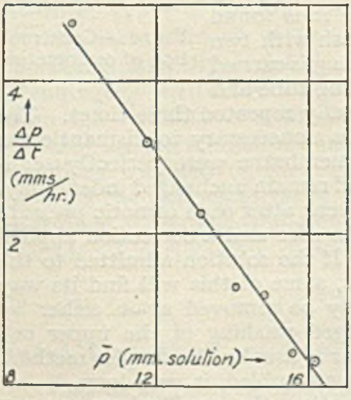

FIG. 2.—Osmotic pressure of gel rubber in benzene + 15 % MeOH at 25° C.

## (b) The Method of Isothermal Distillation.

The vapour pressure lowering produced by dissolving a high molecular substance is difficult to measure directly, but it can be obtained by measuring the rate at which the solvent distils isothermally into the solution. The apparatus used is shown in Fig. 3, and is essentially the same as one described by Signer.[2] It consists of two bulbs 3-4 cm. diameter connected

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[2] *Ann.*, 1930, 478, 246.

by a short wide bridge. Side tubes, subsequently sealed off, are provided for filling and evacuating. Perpendicular to the plane of the bridge and side tubes a measuring tube of *ca.* 4 mm. bore is sealed on to each bulb, its lower end being expanded into an elongated bulb of 3-4 c.c. volume. A reference mark is provided on each measuring tube and the volumes of liquid in the bulbs adjusted so that both levels are in the measuring tubes. The method of working is as follows: Solvent and solution are pipetted into the two bulbs which are then turned into position (*b*), and the measuring tubes cooled in liquid air. One side tube is sealed off, the other constricted and sealed on to the vacuum line. The apparatus is then thoroughly outgassed by successive pumping, melting and freezing: three pumpings suffice, after which the second side tube is sealed off in vacuo and the apparatus mounted in a suitable clamp and placed in the thermostat. The principal error in reading the liquid levels arises from drainage, and it is therefore necessary to standardise the conditions. The apparatus is allowed to warm up in position (*a*), then turned to (*b*) and ½-hour allowed before the levels are read by means of a cathetometer. The apparatus is then returned to position (*a*) for a measured length of time while distillation occurs, after which ½-hour is again allowed in position (*b*) before reading the new levels.

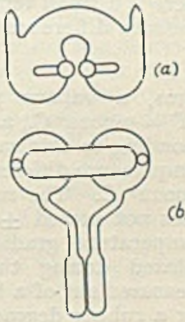

FIG. 3.—Isothermal distillation apparatus.

Signer's method of obtaining molecular weights was to employ instead of pure solvent a solution of known vapour pressure, and to allow distillation to occur until equilibrium was established. This was a very laborious procedure, even though accelerated by periodical thermal distillations in the direction indicated by the isothermal distillation. It was therefore thought desirable to attempt to base calculations on the rate of distillation of pure solvent into the solution and calibration experiments were carried out using solutions of known vapour pressure. These showed that the rate of distillation was proportional to the vapour pressure difference between the two bulbs: the following figures represent a typical calibration. The solute employed was olive oil, which for present purposes may be taken to be triolein, M.W. 885. If $p$ is the vapour pressure of the solvent (benzene) and $\Delta p$ the vapour pressure lowering produced by the solute, $\Delta p/p$ is calculated from the mole fraction of olive oil in the solution. If $R$ is the observed rate of distillation (mms. of measuring tube/hr.) the results are expressed in terms of a constant $k$, given by

$$\frac{\Delta p}{p} = k \, . \, R.$$

TABLE II.—CALIBRATION OF ISOTHERMAL DISTILLATION BULBS FOR BENZENE SOLUTIONS AT 25° C.

| Conc. of Solution, $\frac{\text{gms. Olive Oil}}{\text{100 cc. Solution}}$ | $\Delta p/p$ (calculated). | $R$ (mm./hr.). | $k$ (hr./mm.). |
|---|---|---|---|
| 1·00 | $1{\cdot}02 \times 10^{-3}$ | 0·275 | $3{\cdot}7 \times 10^{-3}$ |
| 0·300 | $3{\cdot}04 \times 10^{-4}$ | 0·074 | $4{\cdot}1 \times 10^{-3}$ |
| 0·100 | $1{\cdot}01 \times 10^{-4}$ | 0·027 | $3{\cdot}7 \times 10^{-3}$ |
| | | Mean | $3{\cdot}8 \times 10^{-3}$ |

The linear relation between $\Delta p/p$ and $R$ is seen from these figures to hold down to $\Delta p/p = 10^{-4}$, *i.e.* an actual difference of vapour pressure of *ca.*

0·01 mm. This represents the lowest value which can be measured with any accuracy : for a 1 % solution this is equivalent to a molecular weight of *ca.* 10,000 and since, as will be shown below, measurements in concentrated solutions are difficult to interpret, 10,000 to 20,000 represents the upper limit of molecular weights measurable by this method. Probably the limiting factor is the accuracy of temperature control which can be achieved. If the two bulbs are both filled with benzene at 25° C. and there is a small temperature difference $\Delta T$ (°C.) between them, the vapour pressure difference is given (from the known $p \sim T$ curve of benzene) by

$$\Delta p/p = 0{\cdot}046\,\Delta T.$$

Thus, a vapour pressure difference of $\Delta p/p = 10^{-4}$ is equivalent to $\Delta T = 0{\cdot}0022°$ C., and in order to measure the isothermal distillation corresponding to this vapour pressure lowering it is essential that any *consistent* temperature difference between the two bulbs shall be small compared with 0·0022° C. The regular fluctuation of the 25° C. thermostat employed does not exceed ± 0·003° C., and in an attempt to minimise the effect of temperature gradients the apparatus has, in later experiments, been rotated during the distillation. The reproducibility attained in the measurement of a fairly high molecular weight is indicated by two figures for a rubber degradation product :—

| Apparatus. | $k$. | Rate of Distillation mm./hr. | $\Delta p/p$. | Mol. Wt. |
|---|---|---|---|---|
| E . . | $3{\cdot}8 \times 10^{-3}$ | 0·037 | $1{\cdot}4_0 \times 10^{-4}$ | 6,700 |
| J . . | $2{\cdot}3 \times 10^{-3}$ | 0·055 | $1{\cdot}5_4 \times 10^{-4}$ | 6,100 |

Although very much faster than Signer's method, the procedure is still somewhat slow, and it was thought possible that the rate-controlling factor was the attainment of equilibrium between the bulk and surface of the liquid. A new form of apparatus was therefore designed, in which the liquid could be shaken during distillation, but the rate of distillation was smaller than usual, due no doubt to the use of a narrower bridge tube. The rate-controlling factor is therefore the diffusion of the vapour, and all that can be done to accelerate distillation is to make the bridge as short and wide as possible. The distillation is not very sensitive to traces of air : introduction of air to a pressure of 6·2 mm. reduced the rate by approximately 50 %.

The method is not likely to find very general application, but it has a number of important advantages for special purposes. Thus it can be used with materials which are unstable in air, since all measurements are conducted in vacuo. Further, it is applicable to any temperature between the freezing and boiling-point of the solvent. For molecular weights between 1,000 and 20,000 it is more accurate than a cryoscopic or ebullioscopic measurement, but for higher molecular weights it must be replaced by direct observation of the osmotic pressure.

## (2) The Viscosity Method.

The basis of the viscosity method is the use of the Staudinger equation,[3] according to which the specific viscosities of dilute solutions of a homologous series of linear polymers are proportional to their molecular weights and to their concentrations

$$\eta_{\text{sp}} = K_m c M.$$

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[3] Staudinger, 1932, "*Die Hochmolekularen Organischen Verbindungen*," Julius Springer.

In practice $\eta_{sp}/c$ is found to be a function of $c$ and it is therefore necessary to measure $\eta_{sp}$ at several concentrations, extrapolate to infinite dilution,* and write

$$M = K \lim_{c \to 0} (\eta_{sp}/c).$$

In order to be able to carry out this extrapolation with precision, measurements must be made of specific viscosities as low as 0·05, so that the viscosities of the solvent and solution must be known with a high relative accuracy. This accuracy is difficult to attain with a rotating cylinder viscometer, and a capillary flow type of instrument has therefore been employed despite its theoretical disadvantages (referred to below).

The viscometers were constructed in pyrex from a design based on that described by Washburn,[5] but were much smaller, the approximate dimensions of a typical model being as follows : Volume of small bulb between reference marks 2 c.c., diameter of liquid surface in large bulb 4 cm., length of capillary 33 cm., radius of capillary 0·35 mm., mean head of liquid during flow 9 cm., total volume of liquid required 8 c.c., flow time for benzene at 25° C. 80 secs.

To measure a specific viscosity of 0·05 correct to 1 % requires each individual viscosity to be accurate to 0·025 %. Variations of 0·025 % would be produced by any of the following errors :—

(1) The change in hydrostatic pressure arising from an error in the volume of liquid used of 0·03 c.c. ; the pipetting error should not exceed this figure.
(2) A temperature variation of 0·01° C. ; the thermostat fluctuation does not exceed ± 0·003° C.
(3) An error of 1·3° in levelling the viscometer. The viscometer is rigidly clamped to a brass rod whose upper end carries a horizontal plate fitted with levelling screws : these are adjusted so as to level the horizontal plate in two directions at right angles. The viscometer is not removed from the clamp for cleaning, so that the levelling is quite reproducible.
(4) An error of 0·02 sec. in timing the flow. The flow is timed by a stop watch making 30 beats per sec. and easily read to 0·03 sec.

A series of 4 or 5 measurements is made and the maximum deviation is usually less than 0·1 sec., with a mean deviation from the average of not more than 0·03 sec.

The overall relative error in the measurement of a viscosity is estimated to be less than ± 0·1 % ; molecular weights can consequently be measured with an accuracy of ± 5 %. In practice this figure is probably improved upon ; the reproducibility of results suggests that an accuracy of ± 2 % is usually attained.

It has on occasion been necessary to measure viscosities in vacuo, and for this purpose a viscometer was constructed as shown in Fig. 4. The solution is poured into the large bulb through the side tube, which is then sealed on to the vacuum line. After outgassing the solution, the side tube

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* It is usually simpler to extrapolate the intrinsic viscosity $[\eta]$, defined as $\frac{1}{c}\log_e(1 + \eta_{sp})$ rather than $\eta_{sp}/c$. These quantities are, of course, identical at infinite dilution, but while $\eta_{sp}/c$ rises rather rapidly with $c$, $[\eta]$, which must always be less than $\eta_{sp}/c$, is often nearly independent of $c$. It is also possible to estimate the intrinsic viscosity at infinite dilution $[\eta]_0$ *approximately* from a single observation at higher concentration by making use of the empirical equation of Philippoff[4] $1 + \eta_{sp} = (1 + [\eta]_0 c/8)^8$. Although this equation holds surprisingly well over a very wide range of concentrations of rubber solutions in toluene (up to 4 %) it is not strictly accurate even for dilute solutions and is therefore of no assistance in extrapolating to infinite dilution.

[4] *Rubber Chem. Tech.*, 1937, **10**, 76.

[5] *J.A.C.S.*, 1913, **35**, 737.

is sealed off and the viscometer mounted in a clamp pivoted about the point A so that the solution can be run from one bulb to the other by tilting the viscometer suitably. It is of course necessary to ensure that the viscometer is always in the same position for measurement: this is accomplished by supporting the pivot from a plate equipped with levelling screws and adjusting the clamp by means of an extension rod fitting into a slot cut out of the plate. The large horizontal displacement of the two bulbs precludes high accuracy, but this was not needed in this particular work.

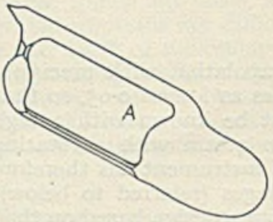

FIG. 4.—Vacuum viscometer.

## Interpretation of Results.

### (*a*) Osmotic Data.

Interpretation of the osmotic pressure or vapour pressure lowering of solutions of high molecular weight compounds is complicated by the fact that such solutions do not in general show ideal behaviour, *i.e.* the osmotic pressure is not proportional to the concentration, but increases considerably more rapidly. If $\Pi$ is the osmotic pressure and $c$ the concentration, the ideal van 't Hoff law has the form $\Pi/c = RT/M$, where $M$ is the molecular weight. In order to eliminate the variation of $\Pi/c$ with $c$, it is necessary to extrapolate to infinite dilution, and write

$$M = RT/\lim_{c \to 0} (\Pi/c).$$

The departure from ideal behaviour is generally ascribed to solvation, the dissolved particles carrying with them so much solvent that their effective concentration is reduced. Provided they are individually solvated, extrapolation to infinite dilution will eliminate this error. Even if association of the particles occurs, measurements in sufficiently dilute solution would be expected to permit an extrapolation to the unassociated state at infinite dilution. The extent of the variation of $\Pi/c$ with $c$ depends on both the solvent and the solute, and all data hitherto published for rubber solutions show particularly large deviations. It is therefore important to have some knowledge of the law relating $\Pi/c$ to $c$, and a number of equations have been suggested. Sackur [6] assumed the volume of solvent removed by solvation to be independent of the solute concentration; his equation may be put in the form

$$\Pi(1/c - b) = RT/M,$$

or

$$\Pi/c = RT/M + b\Pi.$$

Thus $\Pi/c$ should be a linear function of $\Pi$. Meyer and Mark [7] have employed this method to extrapolate their data for crepe solutions. Ostwald [8] suggests that the deviation is to be ascribed to a swelling pressure and adds an empirical correcting term

$$\Pi = \frac{c}{M} \cdot RT + kc^n.$$

The second term has the same form as the expression for the swelling pressure of rubber in a number of solvents found empirically by Posnjak,[9] who obtained values of $n$ lying between 2·48 and 3·33. Carter and Record [10] find Ostwald's equation to hold over a wide range of concen-

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[6] *Z. physik. Chem.*, 1910, 70, 477.

[7] *Ber.*, 1928, 61, 1947.

[8] *Koll. Z.*, 1929, 49, 60.

[9] *Koll. Beihefte*, 1912, 3, 417.

[10] Ref. 1 (*a*).

trations for a large number of polysaccharide solutions, with values of $n$ a little more than 2. Meyer, Wolff and Boissonas[11] show that for solutions of masticated rubber in toluene the equation holds accurately with $n = 2$, so that $\Pi/c$ is a linear function of $c$.

Schulz[12] has modified Sackur's equation by assuming that $b$ can be represented as a function of $\Pi$ by an equation analogous to Posnjak's equation for the swelling pressure. Putting $\Pi = kb^{-n}$ and eliminating $b$ he obtains

$$M = \frac{RTc}{(1 - c^n\sqrt{k/\Pi})}$$

where $n$ should have values of the order of those found by Posnjak. For the purposes of extrapolation this may be more conveniently transformed to

$$\Pi/c = RT/M + K^{\alpha}, \quad \text{where } K = k^{\frac{1}{n}}, \quad \alpha = 1 - 1/n \approx 0{\cdot}5.$$

Hence a plot of $\Pi/c$ against $\sqrt{\Pi}$ should be nearly linear. There are thus three ways of extrapolating $\Pi/c$ to infinite dilution, all of which have been claimed to give nearly linear plots:

$$(1)\ \Pi/c \sim \Pi\,; \quad (2)\ \Pi/c \sim c\,; \quad (3)\ \Pi/c \sim \sqrt{\Pi}.$$

In Fig. 5 the data of Meyer, Wolff and Boissonas have been extrapolated by these three methods, and it is at once evident that (1) can be eliminated. Either of the other plots is linear within experimental error, but they extrapolate to give very different molecular weights, *viz.* from (2) 270,000; from (3) 490,000. Careful consideration of the data shows that these two curves cannot be distinguished experimentally, as the difference occurs almost entirely at very low concentrations, Schulz's equation requiring the $\Pi/c \sim c$ curve to dip sharply downwards for very low concentrations. Schulz claims to have shown this behaviour experimentally for polystyrene solutions, but the evidence is not very convincing. It is to be noted also that his equation requires the solvation to become infinite at infinite dilution, which cannot be true. Furthermore, employing a solvent in which rubber forms solutions which are much more nearly ideal than in toluene, our experimental evidence (Part II) supports Ostwald's form of equation and this is therefore taken to be correct.

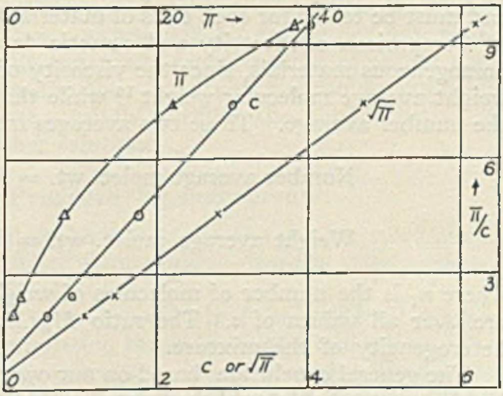

FIG. 5.—Osmotic pressure of milled crepe in toluene.

### (*b*) Viscosity Data.

Staudinger's viscosity equation has been very widely used, but its application requires much greater care than has usually been exercised.

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[11] Ref. 1 (*c*).

[12] Ref. 1 (*b*).

There are two separate points to be discussed: (1) the measurement of specific viscosity, and (2) the relationship between viscosity and molecular weight.

The measurement of the specific viscosity of high molecular substances is complicated by the fact that such solutions show anomalous viscosity, the viscosity becoming lower as the rate of shear is increased. The effect can be eliminated by measuring the viscosity at low rates of shear and extrapolating to zero rate of shear, as has been done by Robinson.[13] In a capillary viscometer the rate of shear is high and varies across the tube, but it has been shown [14] that the specific viscosities of a series of polyvinyl acetates as measured by a capillary viscometer were closely proportional to the corresponding values found with a Couette viscometer at a rate of shear of 1·9 radians/sec. Furthermore, if the specific viscosity of a dilute solution is measured in a series of similar —but not identical—capillary viscometers, the same result is obtained in each. The specific viscosity does, however, depend on the solvent employed, a fact which is undoubtedly related to the varying solvation which occurs in different solvents.

The relationship between viscosity and molecular weight has been the subject of a number of theoretical investigations of which the most complete is that of Huggins.[15] His conclusion is that for dilute solutions of sufficiently long linear molecules the Staudinger law should hold. At present the equation can only be satisfactorily based on experiment, and must be tested for each class of material to which it is to be applied.

Comparison of viscosity and osmotic data is only strictly valid for homogeneous materials, since the viscosity of a mixture depends on the weight average molecular weight [16] while the osmotic pressure measures the number average. These two averages may be defined thus: [17]—

$$\text{Number average molec. wt.} = M_n = \frac{\Sigma n_i M_i}{\Sigma n_i}.$$

$$\text{Weight average molec. wt.} = M_w = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i},$$

where $n_i$ is the number of molecules of weight $M_i$ and the summations are over all values of $i$. The ratio $M_w/M_n$ increases with increasing heterogeneity of the mixture.

The general conclusion, based on our own experiments, supplemented by the most reliable published data, is that the intrinsic viscosity is, to a good degree of approximation, a measure of the molecular weight of a material known to consist of long linear chains, provided that measurements are always made in the same solvent, and are extrapolated to infinite dilution. The Staudinger law does not apply at all to spherical molecules and, in the case of molecules which are only approximately linear (*e.g.* branched molecules), will give the length rather than the molecular weight of the material. It is clear that measurement of the intrinsic viscosity of an unknown material will not necessarily give us the molecular weight: something must first be known about its structure. Alternatively, given its osmotic molecular weight and intrinsic viscosity, some tentative conclusions may be drawn regarding its structure.

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[13] *Proc. Roy. Soc.* (*A*), 1939, **170**, 519.

[14] Cuthbertson, Gee and Rideal, *ibid.*, 300.

[15] *J. Physic. Chem.*, 1938, **42**, 911; 1939, **43**, 439. *J. App. Physics*, 1939, **10**, 700.

[16] Schulz, *Z. physik. Chem.* (*B*), 1935, **30**, 379.

[17] Lansing and Kraemer, *J.A.C.S.*, 1935, **57**, 1369.

## Summary.

A new form of osmometer for use with non-aqueous solutions is described. A method of measuring the vapour pressure lowering produced by a solute from the rate of isothermal distillation of solvent into the solution has been worked out, and shown to be applicable to the measurement of molecular weights up to 10,000. The calculation of molecular weights from the osmotic pressures of non-ideal solutions is discussed. The basis of the viscosity method of determining molecular weights is critically examined.

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# II. OSMOTIC PRESSURE AND VISCOSITY OF SOLUTIONS OF RAW RUBBER.

By G. Gee.

*Received 25th September*, 1940.

Raw rubber is such a variable material that it is not possible to assign to it a definite molecular weight. The value obtained will necessarily differ from sample to sample, although experience shows that this variation is not so large as might have been expected. The absolute values reported in this paper therefore apply only to the particular samples examined, but the order of magnitude will be correct for any similar materials. The object of this paper is to report a series of precise determinations of the osmotic pressure and viscosity of raw rubber and rubber fractions in various solvents, and to consider the application of the Staudinger equation to rubber solutions.

## Osmotic Pressure Measurements.

A number of attempts have been made in the past to calculate the molecular weight of raw rubber from osmotic pressure data; some of the results are given in Table I.

From the last column it is to be noted that two different methods have been employed in extrapolating the data to infinite dilution. Now these methods cannot both be correct, and, as observed in Part I, they may lead to quite different values for the molecular weight. It does not seem possible to resolve the difficulty from the published figures. Plots of $\Pi/c \sim \Pi$, which are linear if Sackur's equation is valid, are actually found to be linear from the data of refs. (2) and (3). Similar plots for the remaining data of Table I are not linear but concave downwards and therefore cannot be extrapolated (*cf.* Fig. 5 of Part I). On the other hand, the data of refs. (1) and (4) can be extrapolated by a linear plot of $\Pi/c \sim c$ (Ostwald's method), while attempts to extrapolate the data of refs. (2) and (3) in this way lead to non-linear plots from which $(\Pi/c)_0$ cannot be accurately estimated. The trouble undoubtedly arises from two sources: (1) the difficulty of measuring accurately the osmotic pressures of dilute solutions, and (2) the wide deviation of the solutions from ideal behaviour. The extent of the latter phenomenon may be seen by calculating the osmotic coefficients of the various solvents in solutions containing 1 g. rubber/100 c.c., *i.e.* the ratio between $\Pi/c$ observed for these solutions and $\Pi/c$ at infinite dilution.[1] The figures

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[1] Guggenheim, *Modern Thermodynamics* (Methuen, 1933), p. 110.

given for these coefficients in Table I have been calculated from the various authors' values of $(\Pi/c)_0$ and are therefore subject to the same errors as those involved in the molecular weight calculation.

It is clear that extrapolation to infinite dilution would be greatly facilitated if a solvent could be found in which rubber formed more nearly ideal solutions. If we accept the view that the non-ideality arises from the removal of free solvent by solvation of the dispersed rubber, the most nearly ideal solvent will be one which produces the minimum of solvation. It is perhaps significant in this connection that the osmotic coefficient of petrol ether was found by Caspari [2] to be less than that of benzene, which is known to be the more active swelling agent for rubber.[6] The search for a more ideal solvent therefore proceeded along two lines: (1) In certain homologous series (*e.g.* the acetic esters) increase in molecular weight is accompanied by a progressive increase in swelling power for rubber. At a fixed temperature there is a line of sharp division between the lower members, which are non-solvents, and the higher members, which dissolve rubber completely.[7] By choosing a liquid just on the solvent side of the line it should be possible to limit solvation to a low value. (2) Addition of a polar non-solvent to concentrated solutions of rubber greatly reduces the viscosity and the phenomenon has been ascribed to desolvation of the rubber particles. The use of mixtures of solvent and non-solvent is therefore worth examination. The three solvents finally examined were—

TABLE I.—Osmotic Molecular Weights of Rubber.

| Material. | Solvent. | Temp. (° C.). | Molecular Weight × $10^{-5}$. | Osmotic Coefficient in 1 % Solution. | Method of Extrapolation to Infinite Dilution. |
|---|---|---|---|---|---|
| Deresinified pale crepe [2] | Benzene . | 25 | $1{\cdot}5_5$ | 2·3 | Ostwald |
| Deresinified pale crepe [2] | Petrol ether . | 25 | $1{\cdot}0_3$ | 1·67 | Ostwald |
| Crepe [3] . | Benzene . | 7 | 3·6 | 1·7 | Sackur |
| Crepe [3] . | Chlorobenzene | 7 | $1{\cdot}8_5$ | 1·43 | Sackur |
| Ether sol from crepe [4] . | Benzene . | 11 | 1·9 | 1·43 | Sackur |
| Ether sol from crepe [1] . | Benzene . | 40 | 1·9 | 1·92 | Sackur |
| Lightly milled crepe [5] . | Toluene . | 24·4 | 2·7 | 4·0 | Ostwald |

(1) Amyl acetate.
(2*a*) Benzene-ethyl alcohol mixtures containing 100 c.c. alcohol/litre.
(2*b*) Benzene-methyl alcohol mixtures containing 150 c.c. alcohol/litre.

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[2] Caspari, *J.C.S.*, 1914, **105**, 2139.
[3] Meyer and Mark, *Ber.*, 1928, **61**, 1947.
[4] Kroepelin and Brumshagen, *ibid.*, 2441.
[5] Meyer, Wolff and Boissonas, *Helv. Chim. acta*, 1940, **23**, 430.
[6] *Cf.* Davis and Blake, *Chemistry and Technology of Rubber* (Reinhold, 1937), p. 184.
[7] *Cf.* for a general account of this phenomenon, Brønsted, *Compt. rend. Lab. Carlsberg, Sér. chim.*, 1938, **22**, 99.

Osmotic pressures of solutions of crepe rubber were measured as described in Part I. Precautions must be taken to prevent oxidation while the solutions are being prepared. The weighed rubber is covered with solvent and the tube cooled in liquid air. After thoroughly outgassing —by successive pumping, melting and freezing—the tube is sealed in vacuo and shaken mechanically until the rubber dissolves. Dilution to the required concentration and subsequent measurement of the osmotic pressure is carried out in air, but solutions are stored in the dark. These precautions have proved adequate in practice, but degradation occurs if solutions are shaken in air or allowed to stand for long periods exposed to air and light.

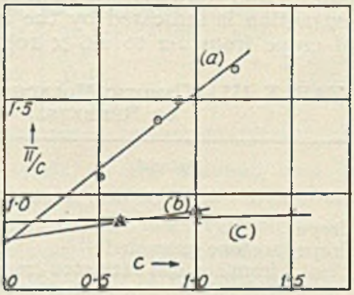

Fig. 1.—Osmotic pressure of crepe solutions at 25° C.

(*a*) Benzene + 10 % EtOH.
(*b*) Amyl acetate.
(*c*) Benzene + 15 % MeOH.

In Fig. 1 the osmotic data are plotted in the form $\Pi/c \sim c$, where $\Pi$ is in mm. Hg and $c$ in g. rubber/100 c.c. solution. The extrapolated values $(\Pi/c)_0$, calculated molecular weight, and osmotic coefficients $g$ of the various solvents in 1 % solutions are collected in Table II :—

TABLE II.—Osmotic Molecular Weights of Crepe at 25° C.

| Solvent. | $(\Pi/c)_0$. | $M \times 10^{-5}$. | $g$ (1 %). |
|---|---|---|---|
| Amyl acetate . . | 0·76 ± 0·05 | 2·4 ± 0·2 | 1·17 |
| Benzene + 10 % EtOH | 0·73 ± 0·10 | 2·5 ± 0·3 | 2·1 |
| Benzene + 15 % MeOH | 0·85 ± 0·03 | 2·2 ± 0·1 | 1·02 |

It is at once apparent that the last solvent gives solutions which are so nearly ideal that the necessity for extrapolation to infinite dilution is largely removed, the molecular weight being directly calculable from the osmotic pressures of solution containing 1 to 1·5 g. rubber/100 c.c. solution. The osmotic coefficient is so near to unity that it becomes doubtful whether the accuracy of the final result is improved by an extrapolation which involves placing equal reliance on the less accurate data for more dilute solutions, and in general molecular weights have been calculated from the osmotic pressures of *ca.* 1 % solutions. The best value for the osmotic molecular weight of crepe at 25° C. is evidently that measured in benzene + 15 % methyl alcohol, *viz.* $2·2 \times 10^5$. The agreement between the molecular weights found in the three solvents is very satisfactory, and confirms the validity of Ostwald's method of extrapolating the data for the solutions in benzene + 10 % EtOH. Schulz's extrapolation formula (applied as in Part I by plotting $\Pi/c \sim \sqrt{\Pi}$) gives for this solvent $M = 4·0 \times 10^5$, and must therefore be definitely ruled out as inapplicable to these solutions, if we assume the molecular weight to be independent of the solvent and equal to the above value of $2·2 \times 10^5$. A plot of $\Pi/c \sim \Pi$, based on Sackur's equation, is only very approximately linear, but cannot be regarded as definitely disproved, since it leads to $M \approx 2·0 \times 10^5$.

Osmotic pressure measurements have been made on several other forms of raw rubber, benzene + 15 % methanol being employed as solvent. The results are collected in Table III.

The "sol" rubber was prepared from acetone extracted crepe by diffusion into petrol ether (60-80). When 40 % had been extracted further separation became very slow, and the remaining 60 % was taken as "gel." Extractions with both acetone and petrol ether were carried out in diffused light and in an atmosphere of nitrogen. Thanks are due to Mr. Grew for specimens of these materials. The rubber fractions were prepared by Dr. G. F. Bloomfield, by the methods described in a recent paper,[8] and were acetone extracted before use. The importance of acetone extraction is indicated by the increase produced in the molecular weight of crepe from 2·2 to $2·6 \times 10^5$. In the case of the low latex fraction the effect was much more marked. Three samples were obtained, in which the acetone extraction had been progressively more severe, and osmotic pressures measured in benzene + 10 % EtOH. It was at once apparent that the three samples were not comparable, so that extrapolation to infinite dilution could not be carried out in the usual way. Use was therefore made of the observation of Buchner and Steutel[9] that the slopes of the $\Pi/c \sim c$ curves for a series of nitrocelluloses were independent of the molecular weight, and the $\Pi/c - c$ curve for the low latex fraction assumed to be parallel to that for crepe: no large error can be introduced by this assumption. The values of $10^{-5} M$ for the three samples were 0·8, 1·3 and 2·1. This effect of acetone extraction is evidently to be ascribed to the removal of low molecular components which would seriously affect the osmotic pressure even if present in small amount, for it was shown that there was no corresponding change in the intrinsic viscosity of the material. The molecular weight of $2·1 \times 10^5$ recorded is naturally to be regarded as less reliable than the figures for the other materials.

TABLE III.—Osmotic Molecular Weights of Rubbers.

| Material. | $M \times 10^{-5}$. |
|---|---|
| Crepe . . . . . . . | 2·2 |
| Crepe (acetone extracted) . . | 2·6 |
| "Sol" from acetone extracted crepe | 3·0 |
| "Gel" from acetone extracted crepe | 2·1 |
| Total latex rubber . . . | 2·8 |
| Hydrocarbon from oxide fraction . | 0·66 |
| Intermediate latex fraction . . | 3·5 |
| Low latex fraction . . . | (2·1) |

It is to be noted that the molecular weight of "gel" rubber is found to be considerably lower than that of "sol," a result which is in direct contradiction to the assumption frequently made that the insolubility of gel rubber in petroleum solvents arises from its high molecular weight.[10] It is evident from the work of Brönsted[7] that high molecular weight is not sufficient to produce insolubility in the case of the polystyrenes, and the present results show that some further mechanism is needed to explain the sol-gel separation.

## Viscosity Measurements.

The viscosities of dilute solutions of crepe in various solvents have been measured as described in Part I, the solutions being prepared in the same way as for osmotic experiments. Measurements were restricted to very dilute solutions and it was in general found that the intrinsic viscosity $[\eta] = \frac{1}{c} \log_e (1 + \eta_{sp})$ was almost independent of the concentration so that extrapolation to infinite dilution to obtain $[\eta]_0$ was readily carried out. Benzene was an exception in this respect, $[\eta]$ rising rapidly with $c$. Some typical results are given in Table IV, in which values of $[\eta]$ are calculated by taking $c$ in g./100 c.c. of solution.

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[8] Bloomfield and Farmer, *I.R.I. Transactions* (in press).

[9] *Proc. Akad. Wetenschappen Amsterdam*, 1933, 36, 2.

[10] Kemp and Peters, *J. Physic. Chem.*, 1939, 43, 1063.

TABLE IV.—INTRINSIC VISCOSITY OF CREPE AT 25° C.

| Solvent. | $c_1$. | $[\eta]_1$. | $c_2$. | $[\eta]_2$. | $c_3$. | $[\eta]_3$. | $[\eta]_0$. |
|---|---|---|---|---|---|---|---|
| Benzene . . . | 0·0352 | 6·95 | 0·0300 | 6·70 | 0·0200 | 6·35 | $5{\cdot}7_5$ |
| Ethylene dichloride . | 0·102 | 3·14 | 0·0500 | 3·14 | 0·0200 | 3·19 | $3{\cdot}1_5$ |
| Amyl acetate . . | 0·098 | 3·52 | 0·049 | 3·40 | | | $3{\cdot}3_0$ |
| Benzene+15% MeOH | 0·0503 | 3·28 | 0·0302 | 3·36 | | | $3{\cdot}4_5$ |
| Benzene+10% EtOH | 0·0588 | 4·95 | 0·0200 | 4·83 | | | $4{\cdot}8_0$ |

The intrinsic viscosity evidently depends on the solvent, and in particular the addition of small amounts of a non-solvent reduces the viscosity considerably. The fact that different intrinsic viscosities are found in different solvents does not necessarily prevent their use in calculating molecular weights, so long as the ratio of the intrinsic viscosities in two solvents is independent of the molecular weight of the material so that a definite Staudinger constant can be applied to each solvent. Table V contains a comparison of some intrinsic viscosities measured in benzene and in benzene + 15 % MeOH, and it will be noted that this relationship holds good.

TABLE V.—EFFECT OF MeOH ON INTRINSIC VISCOSITY OF RUBBERS.

| Material. | $[\eta]_0$ Benzene. | $[\eta]_0$ Benzene + 15 % MeOH. | Ratio. |
|---|---|---|---|
| Crepe . . . . . . | $5{\cdot}7_5$ | $3{\cdot}4_5$ | 0·60 |
| Sol rubber . . . . . | $5{\cdot}7_5$ | $3{\cdot}3_5$ | 0·58 |
| Intermediate latex fraction . | $5{\cdot}8_0$ | $3{\cdot}5_0$ | 0·60 |
| Milled crepe . . . . . | 1·33 | 0·81 | 0·61 |
| Hydrocarbon from oxide fraction | 1·02 | 0·60 | 0·61 |

In calculating the molecular weight by means of the Staudinger equation, it is therefore necessary to employ a separate constant for each solvent employed. Determination of the absolute value of this constant involves comparison with a molecular weight determined in some other way. Staudinger and Bondy [11] compared the viscosity and cryoscopic molecular weights of rubber degradation products, of molecular weight *ca.* 4000, in tetralin and xylene solutions. Expressing the Staudinger equation in the form

$$M = K[\eta]$$

and converting concentrations to g. rubber/100 c.c. of solution, their constants * are found to be

$$\text{Tetralin } K = 2{\cdot}5 \times 10^4.$$
$$\text{Xylene } K = 2{\cdot}9 \times 10^4.$$

From the data of Kemp and Peters [10] for masticated crepe solutions the constants for tetralin, benzene and hexane stand in the ratio 1 : 1·04 : 1·18, and the constant for benzene would then be 2·6 × 10⁴.

[11] *Ber.*, 1930, 63, 734.

* All "Staudinger constants" given in this paper are defined by the equation $M = K[\eta]$ and are therefore inversely proportional to the $K_m$ values usually employed.

Applying this to our data for the intrinsic viscosity of crepe leads to a molecular weight of $1{\cdot}5 \times 10^6$. This is to be compared with the osmotic value of $2{\cdot}2 \times 10^5$ and, in view of the fact that the viscosity molecular weight must, for a non-homogeneous material, be greater than the osmotic value (*cf.* Part I) it is evident that this constant is too small. Considering the very large extrapolation involved, the discrepancy is surprisingly small, but it would clearly be more satisfactory to compare directly the viscosity and molecular weight of a material of high molecular weight. The comparison should ideally be made for a homogeneous material or alternatively the molecular weight used should be a weight average. Lansing and Karemer[12] have compared the weight average molecular weight of sol rubber (determined by ultracentrifuge) with its intrinsic viscosity in ether solution with the following results :—

| $10^{-5} M_W$. | $[\eta]$. | $10^{-4} K$ (Staudinger). |
|---|---|---|
| 4·0 | 4·21 | 9·5 |
| 4·35 | 4·65 | 9·35 |
| | Mean | 9·4 |

The intrinsic viscosity of our sample of sol rubber in ether at 25° C. was measured and found to be 3·65, whence using the above constant its weight average molecular weight is $3{\cdot}43 \times 10^5$.* Having now obtained the molecular weight of "sol" rubber, the Staudinger constants for benzene and benzene + 15 % MeOH can be calculated from the intrinsic viscosities given in Table V. Thence by use of Table IV the constants for the various solvents employed for crepe are calculated. In Table VI these constants are tabulated together with some for other solvents calculated from the ratios between viscosities in different solvents measured by Kemp and Peters.[10]

TABLE VI.—Staudinger Constants for Rubber.

| Solvent. | $10^{-4} K$. |
|---|---|
| Ether . . . . | 9·4 |
| Benzene . . . . | 6·0 |
| Benzene + 15 % MeOH | 10·2 |
| Benzene + 10 % EtOH. | 7·1 |
| Ethylene dichloride . | 10·8 |
| Amyl acetate . . | 10·4 |
| Tetralin . . . . | 5·8 |
| Hexane . . . . | 6·8 |

It is now possible to employ these constants to calculate the viscosity molecular weights of various forms of raw rubber, for comparison with the osmotic data given in Table III. The comparison is made in Table VII, which includes also values of the non-uniformity coefficient $\beta$, as defined by Lansing and Kraemer.[13] In the absence of a precise knowledge of the molecular weight distribution they assume it to be represented by an error function. The number and weight average molecular weights are then calculated in terms of the most probable molecular weight $M_p$ and a single parameter $\beta$ :—

$$\begin{cases} M_n = M_p e^{0\cdot75\beta^2} \\ M_w = M_p e^{1\cdot25\beta^2} \end{cases}$$

whence $$\beta^2 = 2 \log_e M_w/M_n.$$

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[12] Quoted by ref. (6), p. 232.

* Ether is a very unsatisfactory solvent for a viscosity molecular weight standard on two accounts : (1) Its high volatility makes it difficult to make accurate viscosity measurements at 25° C., (2) it very readily develops peroxides which would lead to degradation of the rubber. The solvent used was free from peroxides and the solution was made in vacuo as usual. In order to minimise the effect of evaporation the viscosity determinations were made as rapidly as possible.

[13] *J.A.C.S.*, 1935, 57, 1369.

TABLE VII.—Viscosity and Osmotic Molecular Weights of Rubber.

| Material. | $10^{-5}$ *M*. | | Solvent used for Viscosity Measurement. | *β*. |
|---|---|---|---|---|
| | Osmotic. | Viscosity. | | |
| Crepe | $2{\cdot}2 \pm 0{\cdot}1$ | $3{\cdot}4_5 \pm 0{\cdot}1$ | Benzene | $1{\cdot}0_5$ to $0{\cdot}8_5$ |
| Acetone extracted crepe | $2{\cdot}6 \pm 0{\cdot}2$ | $3{\cdot}4_5 \pm 0{\cdot}1$ | Benzene | $0{\cdot}9$ to $0{\cdot}6$ |
| " Sol " from acet. extracted crepe | $3{\cdot}0 \pm 0{\cdot}2$ | $3{\cdot}4_5 \pm 0{\cdot}1$ | Ether | $0{\cdot}7$ to $0{\cdot}3$ |
| " Gel " from acet. extracted crepe | $2{\cdot}1 \pm 0{\cdot}1$ | $3{\cdot}0_5 \pm 0{\cdot}1$ | Benzene + 15 % MeOH | $0{\cdot}9_5$ to $0{\cdot}8$ |
| Total latex rubber | $2{\cdot}8 \pm 0{\cdot}2$ | $3{\cdot}3 \pm 0{\cdot}1$ | Benzene + 15 % MeOH | $0{\cdot}7_5$ to $0{\cdot}3_5$ |
| *Rubber Fractions.* | | | | |
| Hydrocarbon from oxide fraction | $0{\cdot}66 \pm 0{\cdot}03$ | $0{\cdot}63 \pm 0{\cdot}02$ | Benzene | — |
| Low latex fraction | $2{\cdot}1 \pm 0{\cdot}3$ | $2{\cdot}4 \pm 0{\cdot}1$ | Benzene | — |
| Intermediate latex fraction | $3{\cdot}5 \pm 0{\cdot}2$ | $3{\cdot}5_5 \pm 0{\cdot}1$ | Benzene + 15 % MeOH | — |

These results may now be employed to test the applicability of the Staudinger law to rubber solutions. If the rubber fractions separated by Bloomfield and Farmer were homogeneous, their osmotic and viscosity molecular weights should be equal. Hence, if the Staudinger law holds, the ratio of osmotic molecular weights to intrinsic viscosity in a given solvent should be the same for all the fractions, and equal to the Staudinger constant. If, further, the scale of Staudinger constants drawn up in Table VI is correct, the viscosity molecular weights of the fractions calculated from them should agree with their osmotic molecular weights. It is evident from Table VII that this is true, within experimental error, and we may therefore draw two important conclusions : (1) The Staudinger law holds for rubber solutions *at least* over the molecular weight range 60,000 to 350,000. (2) The scale of constants given in Table VI may be employed to calculate *absolute* weight average molecular weights from intrinsic viscosities measured in dilute solution.

The following consideration suggests that the limits of validity of the Staudinger law are by no means defined by the above figures. Taking the constant obtained for tetralin (Table VI) the viscosity molecular weight of the degraded rubber used as a standard by Staudinger is 8,000, which is to be compared with the cryoscopic value of 3,400. The difference is accountable on the basis of a *β* of 1·3, a not unreasonable value for a degraded product. It appears safe, therefore, to conclude that the Staudinger law holds to a good approximation even down to this molecular weight, and thus to apply it with considerable confidence to less degraded products.

The discrepancy between the osmotic and viscosity molecular weights for non-fractionated rubbers is to be expected on the grounds of their heterogeneity. The progressive approach to homogeneity in the first three materials of Table VII is reflected in the decreasing *β* values, while gel rubber is seen to be much less homogeneous than sol.

## Summary.

The osmotic molecular weight of crepe has been measured in several solvents. It is shown that the use of a "poor" solvent or a mixture of solvent and precipitant gives solutions which approach ideal osmotic behaviour. Benzene containing 150 c.c. methanol/litre is the best solvent examined, 1 % solutions of crepe being almost ideal.

Viscosity data are employed to calculate absolute weight average molecular weights, the Staudinger constant being determined by comparison with ultracentrifuge data. Constants are listed for a number of solvents and shown to vary only by a small factor.

The osmotic and viscosity molecular weights of a number of rubbers are compared; the two values agree for three rubber fractions, while for unfractionated materials the viscosity average is the higher. Non-uniformity coefficients are calculated from the ratio of the two molecular weights.

The molecular weight of "sol" rubber is higher than that of "gel" showing that the sol-gel separation does not arise from molecular weight difference.

The Staudinger law is shown to hold for rubber solutions at least over the molecular weight range 350,000 — 60,000, and probably very much further.

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

The author's thanks are due to Professor E. K. Rideal, who provided facilities at the Laboratory of Colloid Science, Cambridge, for carrying out the early part of this work.

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## REVIEWS OF BOOKS.

**Engineering Physical Metallurgy.** By ROBERT H. REYER. (Chapman & Hall Ltd. 1940. Pp. 549. Price 25s.)

This volume is intended for readers making their first acquaintance with the metals and alloys used in engineering. It covers much of the ground included in text-books of metallography, together with such practical subjects as welding and die casting. It is, however, difficult to make out the plan on which it is arranged. It opens with a single page on space lattices, followed by a detailed account of mechanical deformation and twinning, illustrated by photo-micrographs, with less than a page on fatigue failure. Next follows a short account of equilibrium diagrams, after which comes a chapter on white bearing metals. The light alloys come next, with an account of age-hardening. To a reader who has not previously studied the subject, this must be quite unintelligible. Other alloys, including iron and steel, are treated in successive chapters, and the book contains a large amount of useful information, well illustrated and provided after each chapter with a considerable bibliography. An engineer already having a knowledge of the principles of the subject could turn to this book for information on specific points, especially in regard to American specifications, which are quoted throughout, but a much more logical presentation would be required in a work intended to instruct a user of engineering materials in their essential properties. In particular, a much fuller account of crystal structure would be needed as a preliminary, if the author's plan were to be carried out consistently.

C. H. D.

**Non-Ferrous Foundry Practice.** By J. Laing and R. T. Rolfe. (Chapman & Hall, Ltd. Pp. 336. 1940. Price 21s.)

This treatise on foundry practice in non-ferrous metals and alloys is based on the practical experience of the two authors in their respective works, and this involves certain limitations. These are chiefly seen in the descriptions of methods of melting and casting. The authors are inclined to be conservative in their practice, and the accounts of modern methods, such as the use of the induction furnace, are rather sketchy. In view of the growing use of improved methods, a fuller description of such things as electric furnaces, the Durville method of casting, and recent developments in methods of removing gases, would have been welcomed. On the other hand, moulding processes are well described. A large part of the book is taken up by a survey of the alloys in use in non-ferrous foundries. These are so numerous that it is difficult to see the wood for the trees. The number of alloys recognised in specifications is undoubtedly too large, and it should be possible to introduce simplifications. The authors are particularly interested in the alloys of copper, but the rapidly growing field of light alloys, including those with magnesium as a base, is also fully treated. Some of the alloys mentioned are, however, becoming obsolete.

The illustrations are excellent, and include photo-micrographs of typical structures as well as diagrams.

C. H. D.

**Newer Methods of Volumetric Chemical Analysis.** Edited by Wilhelm Böttger. Translated from the second German edition by Ralph E. Oesper. (London: Chapman & Hall, Ltd. 1938. Pp. xv + 268. Price 18s. 6d.)

This book consists of seven sections written by a number of specialists in the field of analytical chemistry. The subjects and authors are as follows: Elimination of the Titration Error in Acidimetric and Alkalimetric Titrations, by Erna Brennecke; Ceric Sulphate as a Volumetric Oxidising Agent, by N. Howell Furman; Alkaline Permanganate Solution as Volumetric Oxidising Agent, by Hellmuth Stamm; Iodate and Bromate Methods, by Rudolf Lang; Chromous Solutions as Volumetric Reducing Agents, by Erna Brennecke; Oxidation-Reduction Indicators, by Erna Brennecke; and Adsorption Indicators for Precipitation Titrations, by Kasimir Fajans. The names of the writers and of the editor are a sufficient guarantee of the excellence of this book, which fulfills its two chief aims of presenting an exposition of the theoretical principles underlying the newer methods of volumetric analysis, and of giving, as far as possible, directions for carrying out the particular analyses. Each section is provided with a very complete bibliography, and there is an excellent index.

The translator has done his work efficiently, and altogether the book is one which should be available to all chemists who have occasion to employ volumetric analytical methods.

S. G.

**Electrochemistry and Electrochemical Analysis.** By H. J. S. Sand, Ph.D., D.Sc., F.I.C. Volume II. **Gravimetric Electrolytic Analysis and Electrolytic Marsh Tests.** (London and Glasgow: Blackie & Sons, Ltd., 1940. Pp. ix + 149. 5s.)

Dr. Sand is a recognised authority on electrochemistry and has been particularly closely associated for many years with the development of methods of electrochemical analysis. His book is thus endowed with a value, derived from a first-hand knowledge of the subject, which will be appreciated alike by those who teach electrochemistry in schools and colleges, and by those concerned with the technical application of electrochemical analysis.

The first volume, which was published last year, dealt fully with theoretical principles, and its appearance has enabled the author to devote this volume entirely to experimental work. In the first fifty pages he gives detailed descriptions of the apparatus and technique of gravimetric electrolytic analysis, proceeding then to consider in turn the deposition and separation of the metals, the analysis of industrial alloys, internal electrolysis, electrolytic microanalysis and electrolytic Marsh tests. The ground is covered very fully indeed, and furnishes the reader with a selection of analytical methods drawn from the author's own work and from many other sources. In numerous instances a brief critical discussion of a particular method is given, and there are many "practical hints" which contribute largely to the successful working of an analysis. Occasionally, too, the author draws attention to points requiring further investigation. Instructions are invariably sufficiently detailed for use as a laboratory manual, and a great many of the experiments described are suitable for students' exercises.

The author is an enthusiastic exponent of his subject and certainly he could have found no better way of popularising it than giving physical chemists the benefit of his own wide experience. A further volume dealing with Potentiometric and Conductometric Titration, Moisture Determinations by means of Capacitance Measurement and the Electrical Measurement of $p$H is to be published when circumstances permit, and users of the present volume will look forward to its appearance.

H. J. E.

PRINTED IN GREAT BRITAIN AT THE ABERDEEN UNIVERSITY PRESS, ABERDEEN

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