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The Rate of Diffusion of Deuterium

Oxide in Water

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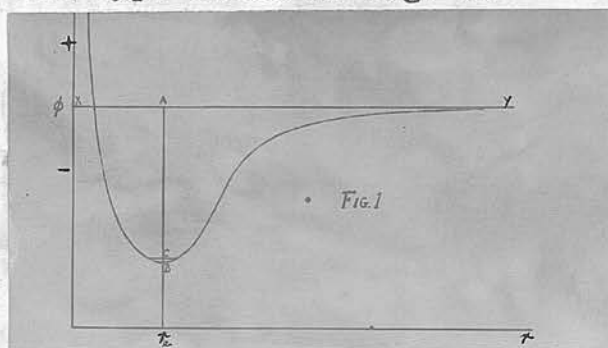
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INTRODUCTION.

Modern atomic theory has shown that the potential energy of any diatomic oscillator as a function of the distance of the atoms apart may be represented by a curve of the type shown in fig. 1.



When the particles are infinitely far apart ($r = \infty$) their potential energy may be taken as zero; thus XY is the abscissa representing zero potential energy. As the internuclear distance, r , is decreased the potential energy of the system at first decreases, due to increasing attractive forces, till, at distances of one or two Ångström units, repulsive forces become increasingly important and as r is decreased these rapidly outweigh the attractive forces so that a minimum occurs in the potential curve at a value, say r_e .

Now quantum mechanics has shown that every oscillator under all conditions - even at absolute zero - possesses a definite quantised residue of kinetic energy. This residual, or, as it is usually called zero-point energy, is equal to $\frac{1}{2} h\nu_0$, where

ν_0 is the ground frequency of the oscillator and ' h ' is Planck's Constant. Thus although the potential energy of the molecule is given by AB (see fig. 1) the energy of dissociation of the molecule (D_v) is $AB - BC$, where BC represents the zero-point energy.

The exact derivation of these potential curves is a rather difficult problem. One method is to apply Condon's theory (Phys. Rev., 28 p.1182 1926) which constructs the curve from the distribution of intensity in the band spectrum. A simpler method, which may be employed when the dissociation energy, the fundamental frequency and the equilibrium radius of the molecule are known, is to determine from these data the constants of the Morse Equation (Phys. Rev. 34, P57), which gives a curve of the required shape. A third method is to determine theoretically the forces involved in the binding of two atoms and, therefrom, to derive an equation for the potential energy. On account of theoretical difficulty this last method is always limited to determining the potential curve accurately around the minimum only so that the quantities D_v and r_e may be obtained with accuracy.

Previous to the development of quantum theory electrostatic calculations had been applied to determine the energies of ionic compounds and crystals (Born, Handbuck der Physik Vol. 24, 1927). These involved a consideration of Coulomb attractive forces, and repulsive forces which were supposed to

arise from multipole interaction.

Now, from a purely formal treatment of the quantum theory (Pauling, J. Am. Chem. Soc., 54 (1), p. 1367), it may be shown, that, for ionic compounds the energy is composed of two parts (1) a Coulomb attractive potential $A(r)$, and a repulsive potential $B(r)$, which results from resonance forces between the electronic shells of the interacting particles. It is thus still justifiable to separate attractive and repulsive forces and to write:-

$$\phi(\bar{r}) = A(r) + B(r)$$

where a proper quantum potential function is used for $B(r)$.

In the case of the electron-pair bond the energy involves several resonance terms (Born, Z.f. Physik. 64, p.729, 1930) mutually interrelated. The quantum treatment of such a problem is very tedious, and has been carried out approximately, only in the very simplest cases (see footnote).

It usually happens however that chemical bonds are not either purely ionic or purely non-polar but, in general, involve a mixture of binding.

FOOTNOTE: H_2 has been treated by Heitler and London, (Z.f. Physik, 44, p. 455, 1927) Sugiura, (ibid, 45, p.484, 1927) and Wang, (Phys. Rev. 31 p. 579, 1928); LiH by Hutchisson and Muskat, (Phys. Rev. 40, p.340, 1932); Li_2^+ and Li_2 by James, (J. Chem. Phys. 2, p.794, 1934) and (ibid, 3, p.9, 1935).

For, if the substitution of an ionic eigenfunction and an electron-pair eigenfunction in the Schrodinger wave equation lead both to about the same energy for the compound, then it follows from quantum mechanics, that a proper solution requires a linear combination of the two eigenfunctions (Pauling, loc. cit.). This substitution always leads to a greater energy than either of the simple substitutions, and thus represents a more stable molecule.

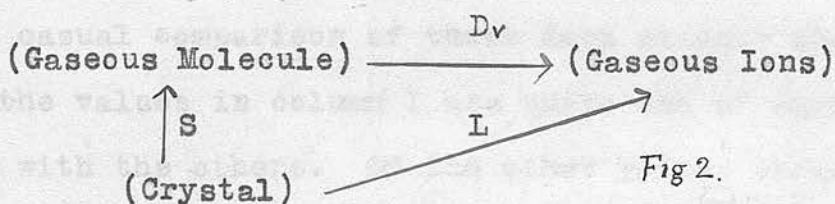
In the following sections the energies of dissociation into ions of the halides of Li, Na, K, Rb, Cs, NH_4 , Cu, Ag, Tl, Au and the hydrides Li, Na, K, Rb, and Cs will be determined first from the experimental data extant, and then reproduced by a theoretical calculation, in which it is assumed that these compounds have a preponderating ionic character.

The sublimation energies of the crystalline salts are not known as precisely although quite a number of independent sets of values have been published.

A complete collection, as far as can be ascertained of the data available for the alkali halides, is given in columns 1, 2, 3, 4, 5 and 6 of table I. The values of Martens² and Bock³ (column 1) and those of Hoshush⁴ (column 5) were determined from measurements of the vapour pressure of the salt at two or more temperatures, the slope of the equation $\frac{d \log p}{dT} = \frac{H}{RT^2}$

Experimental data:- Although the direct experimental determination of the energies of dissociation (D_v) of the gaseous salts mentioned above has not been performed, their values may be obtained indirectly however from the lattice energies (L) and the heats of sublimation (S) of the crystalline salts. From the cyclic process shown in Fig. 2. it is evident that

$$D_v = L - S$$



Values of the lattice energies of all these salts (except those of Au) have been calculated recently by Sherman (Chem. Rev. 11 p.93, 1932) and are estimated to be accurate to within 3%. (See column 2 of table 2). The lattice energies of the aurous salts are those estimated by Klemm (Z.f. physik. Chem. B 12 p.1, 1931).

The sublimation energies of the crystalline salts are not known so precisely although quite a number of independent sets of values have been published.

A complete collection, as far as can be ascertained of the data available for the alkali halides, is given in columns 1,2,3,4,5 and 6 of table 1. The values of Wartenburg and Schulz (column 1) and Fiocch and Rodebush (column 5) were determined from measurements of the vapour pressure of the salt at two or more temperatures, the slope of the equation $\frac{d \log p}{dT} = \frac{S}{RT^2}$

giving the value of S . The values of Klemm, Fajans and Schwartz, Mayer and Helmholtz, Beutler and Levi (columns 2, 3, 4 and 6) and those for the NH_4^+ salts (column 9), which were obtained from data in the I.C.T. and Landholt-Bornstein, were determined from one observation of the vapour pressure which gives the free energy of the change solid (or liquid) \rightarrow vapour, together with the entropies of the solid and vapour which can be estimated from heat capacity data.

A casual comparison of these data at once shows that the values in column 1 are quite out of agreement with the others. Of the other values those in columns 4, 5 and 6 are of greater precision than those in columns 2 and 3. In order now to make an exact analysis of the data the figures must be compared at the same temperature. For this purpose 1 Kilocalorie was calculated to be the average difference in sublimation energy between 0°K . and 298°K . Then placing the greatest reliance on the figures of columns 5 and 6 a weighted mean value was determined, column 7, which in most cases should not be in error by more than 2 K. cals. An exception is LiF which may be in error by 4 K. cals. In the case of the salts of Cu, Ag, Tl and Au reliance had to be placed entirely on Klemm's values (column 8) which may contain an error of 3 K. cals., and, in the case of the alkali hydrides, on Kasarnowski's data which may also be in error by 3 K. cals. Insufficient data was available to calculate a value of (S) for NH_4^+ ; the values for

Table 1.
Heats of Vaporisation of Salts (K.cals / Mol.)

Salt	298° (1)	293° (2)	291° (3)	0° (4)	298° (5)	0° (6)	298° (7)	Salt	293° (8)	298° (9)	K
LiF	57	69	69	62	-	-	67				
LiCl	39	48	49	47	-	-	47	CuCl	23		
LiBr	40	46	47	43	-	-	45	CuBr	23		
LiI	40	51	-	39	-	47	46	CuI	23		
NaF	61	71	72	65	-	-	69	AgF	65		
NaCl	48	58	58	54	-	55	54	AgCl	60		
NaBr	42	51	51	52	54	51	51	AgBr	53		
NaI	39	48	48	48	-	50	48	AgI	46		
KF	45	60	60	59	-	-	59				
KCl	44	53	53	52	52	53	52	AuCl	28		
KBr	41	51	51	50	50	51	50	AuBr	(25)		
KI	39	48	49	48	47	48	47	AuI	(23)		
RbF	43	53	53	54	-	-	53				
RbCl	41	51	50	53	-	-	51	TlCl	37		
RbBr	39	48	49	49	-	-	48	TlBr	32		
RbI	39	48	48	46	-	-	47	TlI	28		
CsF	37	46	46	46	-	-	46	NH ₄ F		-	
CsCl	40	48	49	49	47	-	47	NH ₄ Cl		45	
CsBr	39	48	48	47	-	-	46	NH ₄ Br		51	
CsI	39	48	48	47	-	-	46	NH ₄ I		49	
LiH							(40)				
NaH							27				
KH							22				
RbH							21				
CsH							20				

References to Table 1.

- Column (1) Wartenburg and Schultz, Z. Electrochem. 27
p.568, 1921.
- (2) and (8) Klemm, Z. Physik. Chem. B. 12, p.1,
1931.
- (3) Fajans and Schwartz, Z. Physik. Chem.
Bodenstein Festband, p. 717, 1931.
- (4) Mayer and Helmholtz, Z.F. Physik, 75, p. 26
1932.
- (5) Fiock and Rodebush, J. Amer. Chem. Soc. 48.
p. 2522, 1926.
- (6) Beutler and Lévi, Z. Physik. Chem. B, 24. p.
263, 1934.
- (7) For the alkali hydrides Kasarnowsky, Z.f.
Physik, 61, p.236, 1930.

the other ammonium salts (column 9) do not involve an error larger than 3 K.cals.

The lattice energies, the sublimation energies finally chosen and the energies of dissociation obtained by difference of (L) and (S) are collected in columns 2,3 and 4 respectively of table 2. All the data are in Kilogram-calories per mole and refer to 25°C.

Theoretical Calculation:- The first theoretical calculation of the energies of dissociation of the alkali halides appears to be that of Reis (Zf, Physik, 1 p. 294, 1920), who used the expression

$$\phi = -\frac{e^2}{r} + \frac{be^2}{rn} \quad (1)$$

for the mutual potential ϕ of the ions at the distance r , and employed values of b and n taken from Born's calculation of the lattice energies of salt crystals.

This expression is quite inadequate, since it neglects the important unbalanced polarisation forces which adjacent ions exert on one another. This defect was largely remedied by Born and Heisenberg (Z.f. Physik, 23 p.288, 1924) who derived the expression

$$\phi = -\frac{e^2}{r} \left(1 + \frac{\alpha_+ + \alpha_-}{2r^3} + \frac{2\alpha_+ \alpha_-}{r^6} \right) + \frac{be^2}{rn} \quad (2)$$

In which the polarisabilities α_+ and α_- of the ions are introduced. The values of D_v obtained by these authors agreed very well with the data then available, but when compared with the values given in Table 2 (column 4) are uniformly about 10% too high. This of course might be remedied by a different choice of

constants, but the expression also needs revision because it uses the older crystal lattice repulsive potential.

The application of quantum mechanics to problems involving repulsive potentials by Bruck (Z.f. Physik 51, p. 707, 1928), Unsold (Z.f. Physik, 43, p. 563, 1927) and London, (Z.f. Physik, Ch.B.11, p.222, 1930) has shown that the discriminating part of this potential is exponential in form. Born and Mayer (Z.f. Physik 75, p.1, 1932) have recently applied a repulsive potential of the form $B(r) = b_+ b_- e^{-\frac{r}{\rho}}$ to the calculation of the lattice energies of salts with considerable success. This is applied in a slightly modified form in the following calculation.

The potential energy of the two ions may be expressed as $\phi(r) = A(r) + B(r)$. where $A(r)$ and $B(r)$ are the attractive and repulsive potentials respectively.

$A(r)$ may be written as

$$A(r) = -\frac{e^2}{r} \left(1 + \frac{\alpha_+ \alpha_-}{2r^3} + \frac{2\alpha_+ \alpha_-}{r^6} \right) - \frac{9}{4} \frac{\epsilon_+ \epsilon_-}{\epsilon_+ + \epsilon_-} \frac{\alpha_+ \alpha_-}{r^6}, \quad (3)$$

in which the first term is identical with that of Born and Heisenberg and the second is the resonance term which London (loc.cit) has deduced for the interacting electronic systems. The numerical coefficient $9/4$ suggested by Born and Mayer (loc.cit) has been used instead of $3/2$ as given by London.

Equation (3) can only be applied at temperatures appreciably removed from absolute zero since at very low temperatures, as Margenau (Z.f. Physik, 64, p.584, 1930) has shown, it becomes necessary to modify the

dipole terms.

The repulsive potential of two oppositely charged ions may be written as $B(r) = c_0 b e^{\frac{z_+ z_- - r}{r}}$

c_0 is a numerical constant given by the following formula, due to Pauling (Z.f. Krist., 67 p. 377, 1928)

$$C_0 = 1 + \frac{e_+}{N_+} - \frac{e_-}{N_-} ,$$

where e_+ is the number of electronic charges on the cation and N_+ the number of electrons in its outermost shell, and e_- and N_- refer to the same quantities belonging to the anion. Thus for the Na, K, Rb, Cs and ammonium halides and LiH , $C_0 = 1$, while for Na, K, Rb and Cs hydrides $C_0 = 0.625$, and for $\text{Cu, Ag, Tl, and Au}$ halides $C_0 = 0.929$.

b is a dimensional constant = 10^{-12} ergs. Born and Mayer first assumed r_+ and r_- to be equal to the Goldschmidt ionic radii, and on this basis derived values of ρ from the compressibilities and coefficients of expansion of the crystals. The values obtained for all the alkali halides did not differ greatly and they took for all these salts the mean value $.345 \times 10^{-8}$ cm. The values for the halide salts of the other metals (see footnote) are given in Table 2, column 5.

The values of ρ for silver and thallos salts are given by Mayer (J. Chem. Physics. 1. p. 327, 1933); the value for cuprous salts by Mayer and Levy (ibid 1, p.647, 1933); and the value for ammonium salts by Bleick (ibid 2, p.160, 1934).

Using these values, Huggins and Mayer (J. Chem. Physics I, p. 643, 1933) derived r_+ and r_- more exactly by finding the values required to give agreement with the observed lattice distances of the crystals.

If the values of r_+ and r_- and ρ so obtained, correctly represent the repulsive potential of 2 ions it should be possible to calculate the potential energy at the equilibrium radius (r_e) by first finding r_e from,

$$\phi'(r_e) = 0 \quad (5)$$

and inserting its value in $-\phi(r_e) = D_v + \epsilon$ (6)

where ϵ is the zero-point energy.

The constants of Huggins and Mayer do not, however, give agreement with the experimental values of D_v when used in this way. This is not surprising on account of the complexity of the calculations for crystals since effects, not otherwise accounted for, will appear in the repulsive constants.

It was therefore necessary to determine the repulsive constants ab initio from the experimental material. With the exception of the alkali hydrides, which will be considered later, the value of r_e is unknown and so it is impossible to proceed as Born and Mayer did by inserting its value in (5) to

determine $r_0 = r_+ + r_-$ and calculating D_v by (6) from the values obtained. Assuming that Mayer's values of ρ (loc. cit.) are appropriate both r_e and r_0 can be determined by (5) and (6) using the experimental value of D_v . These values cannot of course be

employed to calculate D_v since they will necessarily reproduce the experimental data, but if the theory is adequate the values of r_o should be additive for different ions. In Table 3 are given the values of r_e and r_o which were obtained for 14 salts. It was then found that when r_e was plotted against r_o (Graph I) that a straight line which represents the relationship

$$r_o = 0.768r_e + 0.824 \quad (7)$$

resulted.

Although no fundamental reason could be found for this equation its importance however, lay in the fact that, having derived it from a limited number of results, one could assume that it held generally for all the halide salts of Li, Na, K, Rb, Cs, NH_4 , Cu, Ag, Au and thereby r_o might be eliminated from (5) and (6). The equations now requiring to be solved on this procedure were:-

$$D_v = \frac{e^2}{r} \left(1 + \frac{\alpha_+ + \alpha_-}{2r^3} + \frac{2\alpha_+\alpha_-}{r^6} \right) + \frac{9}{4} \frac{\epsilon_+ \epsilon_-}{(\epsilon_+ + \epsilon_-)} \frac{\alpha_+ \alpha_-}{r^6} - c_o b e^{\frac{.824 - .232r}{P} - \epsilon} \quad (7)$$

$$\frac{e^2}{r^2} \left(1 + \frac{2(\alpha_+ + \alpha_-)}{r^3} + \frac{14\alpha_+\alpha_-}{r^6} \right) + \frac{27}{2} \frac{\epsilon_+ \epsilon_-}{(\epsilon_+ + \epsilon_-)} \frac{\alpha_+ \alpha_-}{r^7} - \frac{c_o b e^{\frac{.824 - .232r}{P}}}{P} = 0 \quad (8)$$

From these equations the values of r_e and D_v for the alkali, ammonium, cuprous, silver and aurous halides were determined. The agreement between experimental and calculated values of D_v (columns (4) and (7) of Table 2) it will be noted is excellent for all the alkali halides with the exception of LiF and CsF which may be due to faulty experimental data. In the case of the ammonium halides the agreement is

GRAPH 1

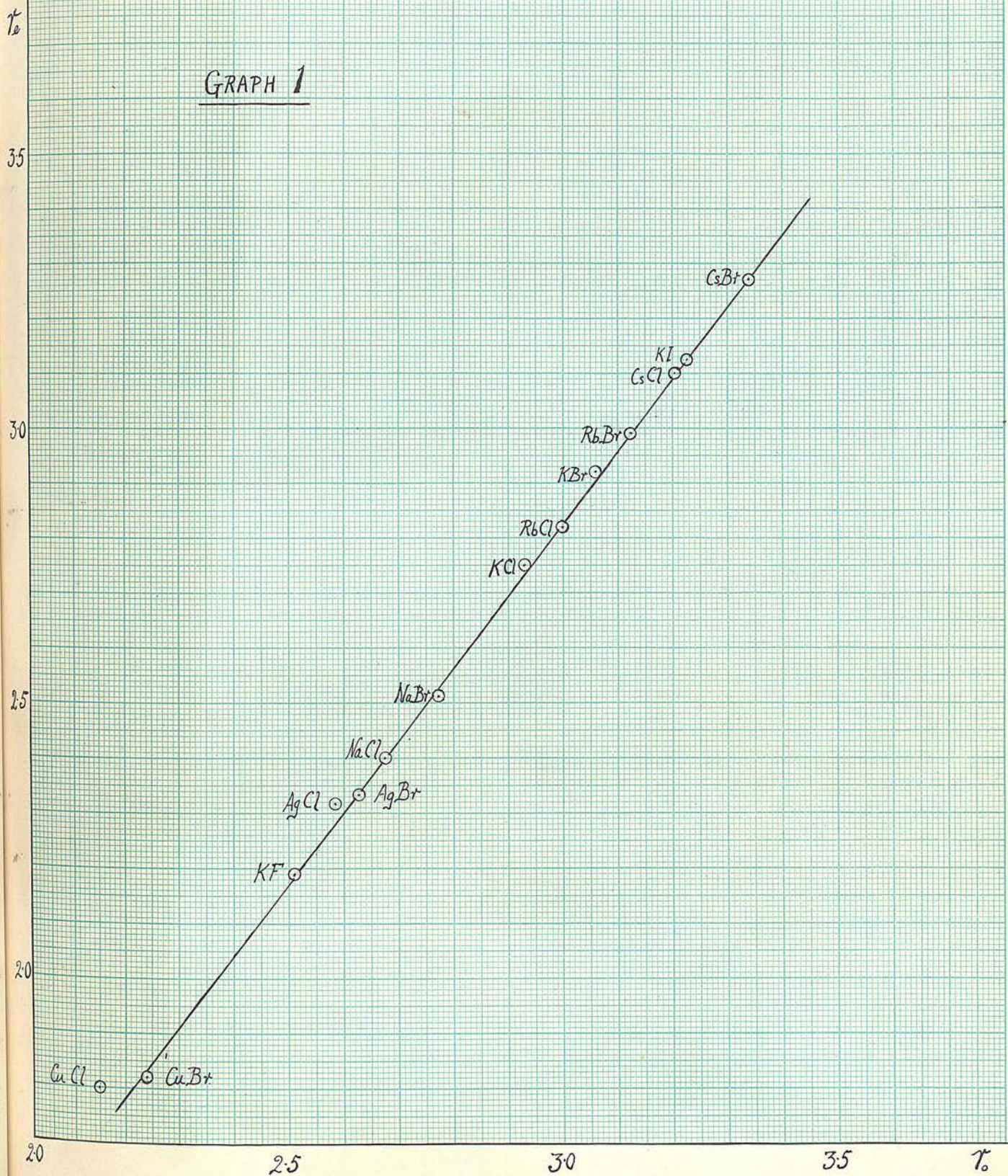


Table 2.

Observed and Calculated Energies of Dissociation.

	L^{25}	S^{25}	D_v^{25}		$r_e(1)$	$D_v(1)$	$r_e(2)$	$D_v(2)$	$\mu \times 10^{18}$ cgs.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
LiF	240.1	67	173		1.598	164	-	>190	5.5
LiCl	193.3	47	146		2.018	147	1.98	150	5.2
LiBr	183.1	45	138	.345	2.138	143	2.15	140	5.1
Li I	170.7	46	125		2.359	135	2.53	126	5.1
Na F	215.0	69	146		1.952	143	1.94	145	9.2
NaCl	180.4	54	126		2.451	124	2.42	124	8.6
NaBr	171.7	51	121	.345	2.610	121	2.63	118	9.0
NaI	160.8	48	113		2.892	110	2.93	109	9.6
K F	190.4	59	131		2.206	131	2.21	133	8.6
K Cl	164.4	52	112		2.704	114	2.69	113	9.9
K Br	157.8	50	108	.345	2.891	108	2.89	108	10.6
K I	149.0	47	102		3.126	102	3.18	100	11.0
Rb F	181.8	53	129		2.345	129	2.33	126	9.0
Rb Cl	158.9	51	108		2.851	109	2.85	109	10.6
RbBr	152.5	48	104	.345	3.009	104	3.00	104	11.1
RbI	144.2	47	97		3.315	97	3.32	97	12.1
Cs F	172.8	46	127		2.566	118	2.61	116	9.7
CsCl	148.9	47	102		3.100	102	3.13	101	11.7
CsBr	143.5	46	97.5	.345	3.270	97	3.27	97	12.3
Cs I	136.1	46	90.9		3.631	89	3.57	90	13.8

Table 2 (contd.)

	L^{25}	S^{25}	D_V^{25}		$r_e(1)$	$D_V(1)$	$r_e(2)$	$D_V(2)$	$\mu \times 10^{18}$ cgs.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
NH_4F	177.5	-	-		2.506	117.5	2.52	116.5	9.87
NH_4Cl	153.3	45	108		3.031	102	3.03	102	11.7
NH_4Br	147.4	51	96	.359	3.199	97.5	3.20	97.5	12.0
NH_4I	143.6	49	94		3.536	90	3.51	91	13.5
LiH	219.2	(40)	179				(1.60)	184.5	-
NaH	192.3	27	165				(1.90)	171	-
KH	168.8	22	147	.345			2.323	143	1.40
RbH	163.3	21	142				2.516	143	3.34
CsH	156	20	136				2.873	118	-
$CuCl$	228.1	23	205		1.738	204	1.74	205	1.82
$CuBr$	223.6	23	201	.223	1.841	201	1.97	185	1.46
CuI	221.2	23	198		2.024	192	2.30	160	-
AgF	223.0	65	158		1.927	165	1.92	166	5.64
$AgCl$	207.3	60	147		2.382	143	2.47	137	6.84
$AgBr$	204.3	53	151	.260	2.514	133	2.65	129	-
AgI	201.9	46	156		2.763	128	2.96	117	-
$AuCl$	236	28	208		1.952	209	1.95	209	2.38
$AuBr$	243	25	218	.200	2.056	202	2.17	186	-
AuI	245	23	222		2.244	190	2.50	159	-
$TlCl$	170.9	37	134				2.30	136	4.41
$TlBr$	166.6	32	135	.361			2.60	123	-
TlI	162.1	28	134				3.04	109	-

again within the possible experimental error. The correspondence in the Table 3. the cuprous, silver and aurous halides will be discussed later.

Salt	r_e	r_0
NaCl	2.40	2.679
NaBr	2.513	2.772
K F	2.19	2.51
K Cl	2.75	2.93
K Br	2.92	3.06
K I	3.126	3.228
RbCl	2.82	3.00
RbBr	2.99	3.123
CsCl	3.10	3.205
CsBr	3.27	3.34
CuCl	1.80	2.15
CuBr	1.82	2.24
AgCl	2.318	2.585
AgBr	2.333	2.628

Using these constants the values of D_v and r_0 for all the salts were recalculated (columns 9 and 10, Table 2). For the alkali and ammonium halides the new values of r_0 required do not differ significantly in the majority of cases from those already obtained. In the case of the Cu, Ag and Au salts quite large differences in r_0 occur due to the fact that equation (7) applies accurately only to a few of these salts

again within the possible experimental error. The correspondence in the case of the cuprous, silver and aurous halides will be discussed later.

Reverting now to our original purpose of determining the repulsive constants r_+ and r_- of individual ions it is evident that these may now be obtained by suitably dividing the values of r_o given by equation (7). In order to determine these constants the value for one individual ion must be chosen.

For this purpose Huggins and Mayer's value of r_- for F^- was taken and the values giving the best additive agreement with r_o for the alkali and ammonium halides were calculated (see Table 4). The values for Cu^+ , Tl^+ and Au^+ were obtained by subtracting the r_- values for the Cl^- ion from the value of r_o for the corresponding chloride. In the case of Ag^+ the r_- value for the F^- ion was subtracted from the r_o value of AgF (see Table 5). The r_o value for Tl^+ , to which equation (7) did not apply, was obtained from the experimental value of D_v .

In Table 6 the values here found are compared with those of Mayer.

Using these constants the values of D_v and r_e for all the salts were recalculated (columns 9 and 8, Table 2). For the alkali and ammonium halides the new values of r_e required do not differ significantly in the majority of cases from those already obtained. In the case of the Cu, Ag and Au salts quite large differences in r_e occur due to the fact that equation (7) applies accurately only to a few of these salts

Table 4.

	r_o	$r_+^+ r_-$	Δ
Li F	2.05	1.96	+ .09
LiCl	2.37	2.35	+ .02
LiBr	2.47	2.48	- .01
Li I	2.64	2.71	- .07
Na F	2.32	2.31	+ .01
NaCl	2.71	2.70	+ .01
NaBr	2.83	2.83	0
Na I	3.05	3.06	- .01
K F	2.52	2.51	+ .01
K Cl	2.90	2.90	0
K Br	3.05	3.03	+ .02
K I	3.23	3.26	- .03
Rb F	2.63	2.62	+ .01
RbCl	3.01	3.01	0
RbBr	3.14	3.14	0
Rb I	3.37	3.37	0
CsF	2.80	2.82	- .02
CsCl	3.21	3.21	0
CsBr	3.34	3.34	0
CsI	3.61	3.57	+ .04
NH ₄ F	2.75	2.76	- .01
NH ₄ Cl	3.15	3.15	0
NH ₄ Br	3.28	3.28	0
NH ₄ I	3.54	3.51	+ .03

Table 5.

$$r_{\text{Cl}^-} = 1.50 \quad r_{\text{F}^-} = 1.11$$

	r_e	r_0	r_+
CuCl	1.738	2.159	0.66
TlCl	-	2.981	1.48
AuCl	1.952	2.322	0.82
AgF	1.927	2.304	1.19

Table 6.

	r_+	r_+ Mayer		r_-	r_- Mayer		r_+	r_+ Mayer
Li ⁺	0.85	0.475	H ⁻	1.66	-			
Na ⁺	1.20	0.875	F ⁻	1.11	1.110	Cu ⁺	0.66	1.183
K ⁺	1.40	1.185	Cl ⁻	1.50	1.475	Ag ⁺	1.19	1.361
Rb ⁺	1.51	1.320	Br ⁻	1.63	1.600	Tl ⁺	1.48	1.272
Cs ⁺	1.71	1.455	I ⁻	1.86	1.785	Au ⁺	0.82	-
NH ₄ ⁺	1.65	1.294 [†]						

† Bleick (J. Chem. Physics 2, p. 160, 1934)

viz. CuCl , AgF and AuCl .

In the case of the alkali hydrides no value of ρ was available, but on the other hand for LiH and NaH the values of r_e and also the fundamental vibration frequencies (ν_0) are known (Krebs. Z.f. Physik, 80, p. 134, 1932).

The values of ν_0 are related to the second derivative of the potential by the equation

$$\nu_0 = \frac{1}{2\pi} \sqrt{K/\mu} \text{ sec}^{-1}, \quad (14)$$

where $K =$ restoring force per unit displacement $=$

$$\phi''(r_e); \mu = \text{reduced mass of the molecule} = \frac{M_+ M_-}{M_+ + M_-},$$

M_+ and M_- being the masses of the two ions concerned,

hence since
$$A'(r_e) = \frac{c_0 b}{\rho} e^{\frac{r_+ + r_- - r_e}{\rho}} \quad (15)$$

and
$$\phi''(r_e) = +A''(r_e) + \frac{c_0 b}{\rho^2} e^{\frac{r_+ + r_- - r_e}{\rho}} \quad (16)$$

$$\therefore \rho = \frac{A'(r_e)}{4\pi^2 \nu_0^2 \mu - A''(r_e)} \quad (17)$$

Having obtained the value of ρ from (17)

substitution in (15) gives $(r_+ + r_-)$. Then using

the values of r_+ for Li^+ and Na^+ already obtained

one obtains the value of r_-

In case of LiH $r_e = 1.60 \text{ \AA}$ $\rho = .3109 \text{ \AA}$
 $\nu_0 = 1383 \text{ cm}^{-1}$ Hence $r_- = 1.72 \text{ \AA}$

In case of NaH $r = 1.90 \text{ \AA}$ $\rho = .3597 \text{ \AA}$
 $\nu_0 = 1171 \text{ cm}^{-1}$ Hence $r_- = 1.65 \text{ \AA}$

Since these values of ρ do not vary considerably

from .345 this value was taken for all the hydride salts. Choosing $\rho = .345$ and solving equation (15) for r_{-} in the case of NaH the value obtained is 1.66.

The values of D_v and r_e obtained using these constants, $\rho = .345$, $r_{-} = 1.66$, are given in columns 9 and 8 of Table 2.

The data used in these calculations are given in Table 7. The polarisabilities are those given by Mayer and Helmholtz (Z.f. Physik, 75, p.19, 1932) together with Pauling's values for Cu^{+} , Ag^{+} , Au^{+} and H^{-} (Proc. Roy. Soc. A 114, p.181, 1927) and a value for NH_4^{+} estimated by Bleick (loc. cit.).

The ionisation potentials of the ions and the electron affinities of the halogens (given in ergs $\times 10^{+12}$) are from a paper by Rabinowitch and Thilo (Z.f. physik. Chem. B.6.p290, 1930): the value for H^{-} is from Sherman's paper (loc. cit.). No value of ρ has been given for Au^{+} . The value used (.200) was estimated by plotting the values for Cu^{+} , Ag^{+} , Tl^{+} against the compressibility of the metal and taking the value corresponding to the compressibility of gold.

Table 7.

	$\alpha \times 10^{24}$ cc.	$E \times 10^{12}$ ergs		$\alpha \times 10^{24}$ cc.	$E \times 10^{12}$ ergs		$\alpha \times 10^{24}$ cc.	$E \times 10^{12}$ ergs.
Li^+	0.079	119	H^-	10.08	1.13	Cu^+	0.43	32.6
Na^+	0.21	75	F^-	1.05	6.5	Ag^+	1.72	33.4
K^+	0.88	50	Cl^-	3.66	6.0	Tl^+	1.87	42.5 (est)
Rb^+	1.41	43	Br^-	4.77	5.6	Au^+	3.50	33.1
Cs^+	2.50	42	I^-	7.10	5.2			
NH_4^+	1.70	45.3						

Numerical Solution of the equations: Since no direct method is available for solving an equation of the type $\phi'(r) = 0$ the value of r required was found by a method of successive approximation.

The initial problem of determining the repulsive constants from the experimental values of D_v was solved in the following way.

Writing equation (5) as

$$A'(r_e) - c_0 b e^{\frac{r_0 - r_e}{\rho}} = 0$$

we obtain by rearranging ,

$$r_0 = 2.303 \cdot \rho \cdot \log_{10} \frac{A'(r_e)}{c_0 b} + r_e$$

Successive values of r_e were now chosen, r_0 calculated, and then r_e and r_0 substituted in equation (6) viz.

$$D_v = A(r_e) + B(r_e) - \epsilon$$

and D_v determined for each value of r chosen. This process was continued till a value of r_e (and thus r_0) was obtained which gave the experimental value of D_v to within 0.5 K.cals. (see Table 3).

Having obtained the relation (7) from these results the equation $\phi'(r_e) = 0$ was now solved directly for r_e in the following way.

A reasonable value of r_e (say r_1) was chosen and $A'(r_1)$ and $B'(r_1)$ evaluated.

If $A'(r_1) + B'(r_1)$ was positive a slightly higher value of r_e was chosen (r_2) and $A'(r_2) + B'(r_2)$ evaluated.

This process was continued till $A'(r_e) + B'(r_e) = 0$.

This method is not so laborious as might at first

sight appear as an actual example chosen at random will show.

$$\begin{aligned} \text{NH}_4\text{Br} \quad r_1 &= 3.162 && \text{ergs} \times 10^{-12} \\ A'(3.162) + B'(3.162) &= 3.639 - 3.583 = + .056 \\ r_2 &= 3.18 \\ A'(3.18) + B'(3.18) &= 3.572 - 3.542 = + .030 \\ r_3 &= 3.236 \\ A'(3.236) + B'(3.236) &= 3.368 - 3.416 = - .048 \\ r_4 &= 3.199 \\ A'(3.199) + B'(3.199) &= 3.500 - 3.498 = + .002 \end{aligned}$$

Hence r_e for $\text{NH}_4\text{Br} = 3.199$.

In every case a solution was obtained where $A'(r)$ differed from $B'(r)$ by not more than 0.1%.

From these values of r_e the energies D_v were calculated by direct substitution in equation (6).

The zero-point energy \mathcal{E} was calculated from the equation $\mathcal{E} = \frac{1}{2} h\nu_0$ (ergs) in certain cases, where

$$\begin{aligned} h &= \text{Planck's constant} = 6.55 \times 10^{-27} \text{ (erg.-secs)} \\ \text{and } \nu_0 &\text{ is given by equation (14) above.} \end{aligned}$$

Its magnitude in the case of the alkali halides varies from .2 Kcals for CsI to 0.8 Kcals for LiF.

Since these values are within the experimental error, a deduction of .5 Kcals was made in every case for the alkali, NH_4 , Cu, Ag, Tl and Au halides. In the case of LiH, \mathcal{E} has a value of 2.0 Kcals and in NaH, a value of 1.7 Kcals. A deduction of 1 Kcal was made in the case of the other hydrides.

The values of r_e determined from the additive constants (column 8 Table 2) were calculated

approximately (to within 1%) by plotting $\phi(r)$ as a function of r , the minimum in the curve giving both r_e and D_v

column (4), in the case of the alkali and ammonium halides it is evident that both calculations give satisfactory results. The exception is NaF which may be due to faulty experimental data, another is MgF_2 , for which the second method of calculation fails to give a definite result.

In every other case the calculations agree within the possible experimental error. It would appear to be justified therefore to classify these compounds as purely ionic.

Further evidence of the adequacy of the calculations comes from a comparison of the calculated values of r_e with values of r_e for these compounds which may be obtained from a set of ionic radii for molecules compiled by Redbach (Trans. Far. Soc. 32, p. 782, 1934). Redbach points out that these molecular radii do not give exactly additive ionic radii so that the values obtained are only rough averages. The general agreement shown in Table II is however satisfactory.

The calculations in the case of the transition metal halides fails to account even for the sequence of values in these salts. The experimental values of the alkali halides (fig. 3) all decrease in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$, while for the transition metal salts either increase in the order $\text{Cl} < \text{Br} < \text{I}$ or (in cuprous salts) decrease to a much smaller extent than in the case of the alkali halides.

Discussion:- From a comparison of the calculated values of D_v , columns (7) and (9), and the experimental column (4), in the case of the alkali and ammonium halides it is evident that both calculations give satisfactory results. One exception is CsF which may be due to faulty experimental data, another is LiF, for which the second method of calculation fails to give a definite result.

In every other case the calculations agree within the possible experimental error. It would appear to be justified therefore to classify these compounds as purely ionic.

Further evidence of the adequacy of the calculations comes from a comparison of the calculated values of r_e with values of r_e for these compounds which may be obtained from a set of ionic radii for molecules compiled by Rodebush (Trans. Far. Soc. 30, p. 782, 1934). Rodebush points out that these molecular radii do not give exactly additive ionic radii so that the values obtained are only rough averages. The general agreement shown in Table 8 is however satisfactory.

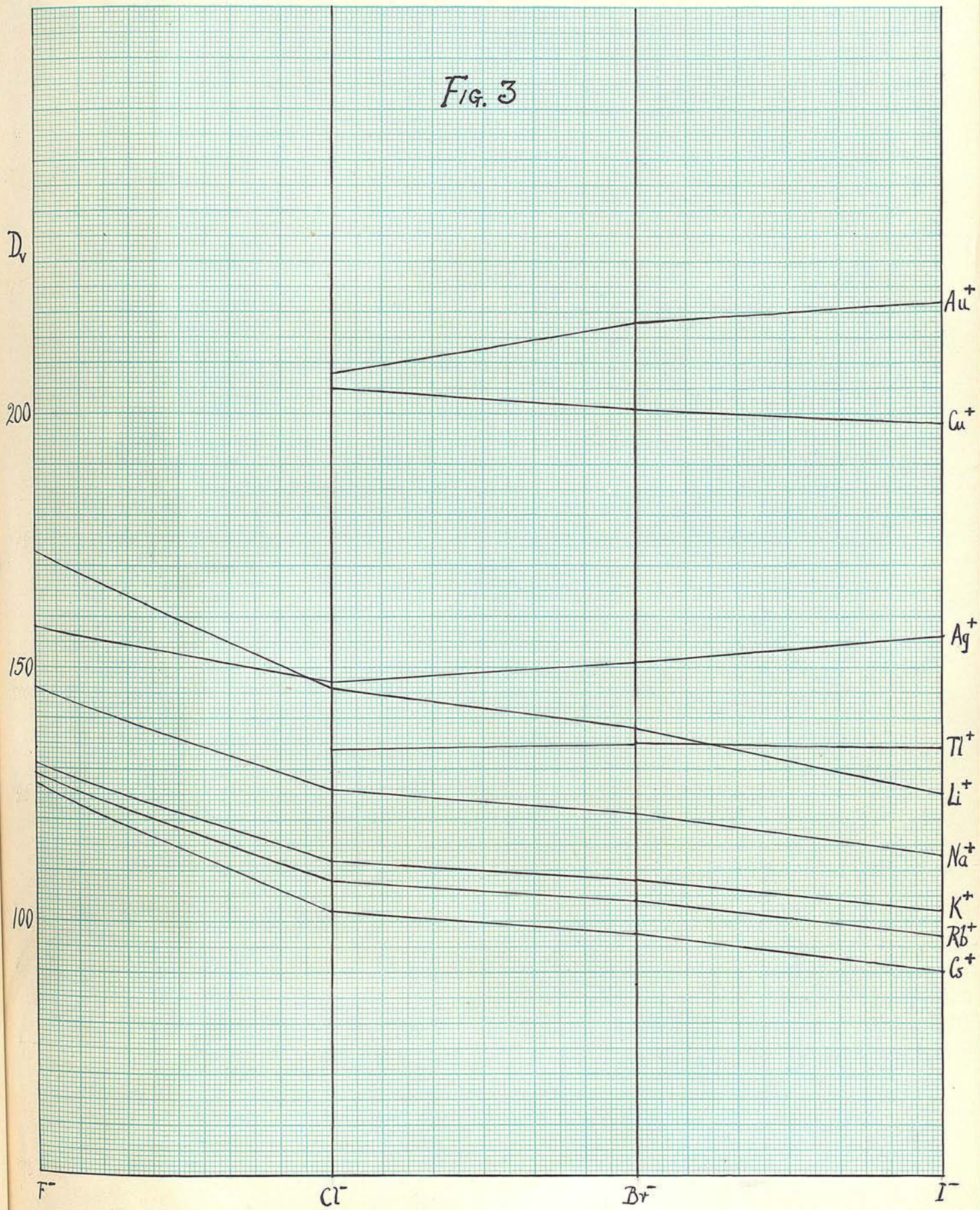
The calculations in the case of the transition metal halides fails to account even for the sequence of values in these salts. The experimental values of the alkali halides (fig. 3) all decrease in the order $F > Cl > Br > I$, while the values for the transition metal salts either increase in the order $Cl < Br < I$ or (in cuprous salts) decrease to a much smaller extent than in the case of the alkali halides.

Table 8.Rodebush.

Ion	Li ⁺	Na ⁺	K ⁺	H ⁻	F ⁻	Cl ⁻	Br ⁻	I ⁻
r	.47	.87	1.18	1.1	1.11	1.47	1.10	1.78

	.Rodebush.	Calc.	Δ
LiH	1.57	(1.60)	- .03
LiF	1.58	1.60	- .02
LiCl	1.94	2.02	+ .08
LiBr	2.07	2.14	+ .07
LiI	2.25	2.36	+ .11
NaH	1.97	(1.90)	+ .07
NaF	1.98	1.95	- .03
NaCl	2.34	2.45	+ .11
NaBr	2.47	2.61	+ .14
NaI	2.65	2.89	+ .24
KH	2.28	2.32	- .04
KF	2.29	2.21	- .08
KCl	2.65	2.70	+ .05
KBr	2.78	2.89	+ .11
KI	3.06	3.13	+ .07

Fig. 3



The calculated values also decrease in the order $F > Cl > Br > I$ in both groups irrespective of the magnitude of the characteristic constants of the metal ions. It is thus evident that salts in the second group are influenced by factors which do not come into the calculation and they cannot therefore be regarded as having purely ionic molecules.

The agreement of the calculated values of the chlorides of these metals given in table 2 column (9) cannot be taken as evidence that these salts are ionic compounds since the repulsive constants of the metals were chosen to give agreement for these salts; but it is evident that if the calculated values of the chlorides are also too high for the ionic bond those of the bromides and iodides will deviate to an even greater extent from the experimental values than those given. Approximate agreement for some of these salts is obtained by the first method of calculation, in which in place of empirical constants, the empirical relation (7) is used. This certainly works for the alkali and ammonium halides and might be regarded as evidence of the ionic nature of the other salts with which it succeeds. But its application to these compounds may be accidental. We can conclude that the energies of dissociation of the bromides and iodides of the transition metals under discussion are certainly greater than is required for ionic binding and are determined largely by other factors, such as occur in the homopolar

bond. These effects occur to a considerably smaller extent, if at all, in the fluorides and chlorides. This fits in with the general conclusions as to the nature of these compounds drawn from spectroscopic (Spooner, Z.f. Electrochem., 34, p.483 1928) and crystallographic evidence (Mayer, J. Chem. Physics 1, p.327, 1933) and from the electrical conductivities of the pure salts (von Hevesy, Z.f. Electrochem., 34, p.463).

In the case of the alkali hydrides it is surprising that so large a measure of agreement exists between experimental and calculated values since it is definitely recognised that these compounds are of a mixed bond type (Rodebush loc. cit).

Moreover the onus cannot, in this case, be laid on the choice of repulsive constants since these have been obtained from experimental material (viz. r_e and γ_0). The choice of $\rho = .345$ may appear to be rather arbitrary. If however the value .3594 (that for NaH) had been chosen the agreement would still be as good as may be seen from the following Table 9.

Table 9.

$$\rho = .3594 \quad r_e = 1.65$$

	D_v exp.	D_v Calc.
NaH	165	165
KH	147	146
RbH	142	135

In a recent communication Hellmann (J. Chem. Physics 3, p.161, 1935) has described a quantum mechanical calculation of the energy of KH in which account is taken both of the ionic binding, which is as large as 80%, and the atomic binding which is 20% of the total binding energy. The preliminary results are compared with those here calculated and with the experimental values in Table 10.

Table 10.

KH

	Hellmann	Thesis	Exptl.
D K.cals	44.8	59.8	63.8
r_e	1.9	2.32	2.31 [†]

† spectroscopic value

Here D is the energy of dissociation of the gaseous molecule into atoms and is related to D_v as follows

$$D = D_v - I + E ,$$

where I is the ionisation potential of K (= 99.6) and E the electron affinity of hydrogen (= 16.4).

From the above Table it is evident that the present calculation fits the experimental facts more exactly than does the present quantum mechanical treatment of Hellmann, even though the latter rests no doubt on a fundamentally more adequate basis.

There are two possible ways by which to explain the agreement thus obtained from these partly homo-polar salts. Firstly it may be that the repulsive potential increases too slowly at ^{small} internuclear

distances and so corrects for the 20% homopolar binding in these compounds or secondly, and more probably, it may be that the value of the polarisability of H^- (10.08) calculated by Pauling is too large. The fact that the calculated moments of LiH and NaH (see below) would appear to be negative seems to justify the second possibility.

where $p_p = e r_p$ and to the first approximation the induced moments in the ions are $p_+ = \alpha_+ e/r_0^2$ and $p_- = \alpha_- e/r_0^2$, so that

$$p = e r_0 \left(1 - \frac{\alpha_+ + \alpha_-}{r_0^2} \right)$$

The values of p so obtained from the calculated values of r_0 are given in Table 2 column 10 for all the salts for which the observed and calculated values of D_v are in reasonable agreement.

For the halides of Ba, K, Rb, Cs and NH₄ the effective moment is of the order of 10×10^{-18} esu units in agreement with the experiments of Wade on these compounds (Z. f. Physik, 14, p.261, 1927).

Lithium salts, AgF and AgCl have values of about half as great, the induced moments being 25% greater than in the previous group, while in the case of cuprous salts, AuCl and the alkali hydrides the induced dipoles are almost as great as the principal dipole. (Indeed in the case of LiH and NaH the calculation fails since here $\frac{\alpha_+ + \alpha_-}{r_0^2} > 1$, whence p would be negative which is impossible).

It will be evident from the above calculations that, in the case of inorganic salts, the dipole

Dipole Moments: An interesting sidelight on the nature of molecules is obtained by calculating their dipole moments. When the calculated value of D_V agrees with that observed it may be considered that the value of r_e is also correct; the effective dipole moment of the salt molecule is then given by:-

$$\mu = \mu_p - (\mu_+ + \mu_-)$$

where $\mu_p = e r_e$ and to the first approximation the induced moments in the ions are $\mu_+ = \alpha_+ e/r_e^2$, and $\mu_- = \alpha_- e/r_e^2$, so that

$$\mu = e r_e \left(1 - \frac{\alpha_+ + \alpha_-}{r_e^3} \right)$$

The values of μ so obtained from the calculated values of r_e are given in Table 2 column 10 for all the salts for which the observed and calculated values of D_V are in reasonable agreement.

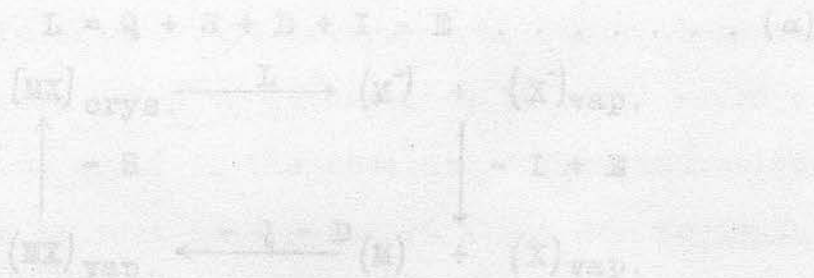
For the halides of Na, K, Rb, Cs and NH_4 , the effective moment is of the order of 10×10^{-18} cgs. units in agreement with the experiments of Wrede on these compounds (Z.f. Physik, 44, p.261, 1927).

Lithium salts, AgF and AgCl have values of about half as great, the induced moments being 25% greater than in the previous group, while in the case of cuprous salts, AuCl and the alkali hydrides the induced dipoles are almost as great as the principle dipole. (Indeed in the case of LiH and NaH the calculation fails since here $\frac{\alpha_+ + \alpha_-}{r_e^3} > 1$, whence μ would be negative which is impossible).

It will be evident from the above calculations that, in the case of inorganic salts, the dipole

moment does not give a quantitative measure of the extent of ionic binding in a compound. From a broad survey of the results it could be concluded that compounds having a moment equal to, or greater than, 5×10^{-18} cgs. units were well defined ionic salts, while those having a lower value might possibly, although not necessarily, involve electron-pair binding.

By means of the following Born cycle the Lattice energy can be expressed as a sum of various thermal quantities namely,



where Q = Heat of formation of [MX] from (M) + $\frac{1}{2}X_2$ in vapour phase

S = Sublimation Energy of crystal [MX]

B = Energy of Dissociation of $\frac{1}{2}X_2$ into (X) atoms

I = Ionisation potential of metal atom (M)

E = Electron affinity of halogen atom (X)

Since all these quantities except the electron

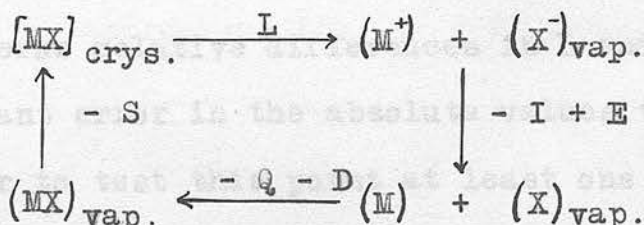
Appendix I

Concerning the Use of Sherman's Values of the γ for
the halogen compounds. Lattice Energies (L)

In determining the so-called experimental values of D_V from the equation $D_V = L - S$ it was necessary to employ calculated values of L, experimental values of L for only 4 salts being so far determined. It is now necessary to show by an indirect appeal to experimental data how it is possible to determine that the values used will agree with the experimental to within 3% as has been stated.

By means of the following Born cycle the Lattice energy can be expressed as a sum of various thermal quantities namely,

$$L = Q + S + D + I - E \dots \dots \dots (\alpha)$$



where Q = Heat of formation of $[MX]$ from $(M) + \frac{1}{2}X_2$ in vapour phase

S = Sublimation Energy of crystal $[MX]$

D = Energy of Dissociation of $\frac{1}{2}X_2$ into (X) atoms

I = Ionisation potential of metal atom (M)

E = Electron affinity of halogen atom (X)

Since all these quantities except the electron

affinity, E , are known with precision for all the alkali halides one may substitute calculated values of L in equation α and so determine values of E for the halogen concerned. If this type of calculation is made with the 20 alkali halides 5 values of E for each halogen are obtained, which, if they are constant yield a definite proof of the adequacy of the calculation in reproducing the experimental change in L with change of cation. (Presumably also the calculation will be as adequate in reproducing the correct changes in L for various anions with a given cation) In the case of Sherman's calculations the largest variations of E from the mean value are for F, Cl, Br, and I, 0.9, 2.7, 2.5 and 2.6 (K.cals.) respectively. These differences represent maximum errors in L of from .5% to 2%.

This test is not however completely adequate since it concerns relative differences in L and would conceal a constant error in the absolute values themselves. In order to test this point at least one accurate experimental value of L is required.

Mayer (Z. Physik, 61, p. 798, 1930) first succeeded in measuring lattice energies experimentally and obtained the values given in table I for KI and CsI. These values may contain the rather large experimental error of ~ 8.0 K.cals. Recently however Mayer and Helmholtz (J. Chem. Physics, 2, p. 245, 1934)

have greatly improved the experimental technique and obtained values for RbBr, and NaCl (given below) which are accurate to ± 3 K.cals.

Table I

	Mayer	Sherman
KI	153.8	149.0
CsI	141.5	136.1
RbBr	151.3	152.5
NaCl	181.3	180.4

It is evident from this table that, in the case of the reliable values for RbBr and NaCl, Sherman's values agree to within 0.8%.

Taking into account the maximum error of 2% indicated by consideration of the consistency of the electron affinity values it would seem that the estimate of an inclusive error of 3.0% was adequate.

Considering the idealized picture of a molecule used in the calculation it will be realized that the expression is solely an approximation formula. The following evidence indicates that it gives values of which are 20-50% too low.

(1) The potential energy of two halogen molecules has been calculated with a high degree of precision by Slater and Kirkwood (Phys. Rev., 37, p. 684, 1931). Their value of the attractive potential is 20% greater than that obtained using formula I.

Appendix II

Concerning the Use of the Coefficient $9/4$ instead of $3/2$ in the London Resonance Expression.

In order to apply quantum mechanical theory to the problem of molecular forces, London in his fundamental paper (Z. f. physik. Ch., B, 11, 1930) considers the interaction of dipoles and obtains the expression

$$\xi = 3/4 \frac{h\nu_0}{R} \alpha^2 \dots \dots \dots (1)$$

for the energy of two similar dipoles R Ångs. apart and having a polarisability α and ground frequency ν_0 (energy $h\nu_0$). For two dissimilar dipoles 1 and 2, R_{12} Ångs. apart, the expression becomes,

$$\xi = 3/2 \frac{h\nu_1 \cdot h\nu_2}{h\nu_1 + h\nu_2} \cdot \frac{\alpha_1 \alpha_2}{R_{12}^6} \dots \dots \dots (1a)$$

Considering the idealised picture of a molecule used in the calculation it will be realised that the expression is solely an approximation formula. The following evidence indicates that it gives values of which are 20-50% too low.

(1) The potential energy of two helium molecules has been calculated with a high degree of precision by Slater and Kirkwood (Phys. Rev., 37, p. 682, 1931). Their value of the attractive potential is 20% greater than that obtained using formula 1.

(2) Born and Mayer (Z. Phys., 75, p. 1, 1932), discussing the use of equation 1 for their calculations, state that, "it would not surprise us if it were later proved from experimental facts that the c-Values $\left[c = 3/2 \frac{h\nu_1 \cdot h\nu_2}{h\nu_1 + h\nu_2} \cdot \alpha_1 \alpha_2 \right]$, thus determined, were about 50% too small."

(3) Bernal and Fowler (J. Chem. Phys., 1, p. 515, 1933) in calculating the resonance energy between two water molecules also consider equation 1 too small and increase the coefficient from 3/2 to 9/4 (i.e. by 50%).

(3) With the above evidence in mind it was considered probable that an alteration of London's coefficient from 3/2 to 9/4 would give a more exact value for the resonance potential. An uncertainty of $\pm 25\%$ in ϵ would of course be serious when this energy was an important factor in the binding. Fortunately in the case of the present calculations it varied only from 0.5% of A (r) for Li salts to 1.7% of A (r) for Cs salts and consequently the uncertainty does not impair materially the results finally obtained.

Possibly not at S U M M A R Y.

(1) The energies of ionic dissociation (D_v) of the halides and hydrides of the alkali metals, and the halides of copper, silver, thallium and gold have been obtained from experimental data.

(2) A theoretical expression for the energies of these compounds has been derived: it differs from that of Born and Heisenberg by the introduction of (1) the London resonance term, and (2) an exponential form of the repulsive potential similar to that used by Born and Mayer for crystals.

(3) A relation is obtained from the experimental material by which the only unknown constant in the repulsive potential is eliminated. The interionic distances of the salts are then calculated and also ~~their~~ energies of dissociation. Good agreement is obtained between the experimental and calculated values of D_v in the case of the alkali halides and several transition metal salts.

(4) Single repulsive exponents for each ion are then evaluated and the energies of dissociation recalculated. The agreement is again satisfactory in the case of the alkali halides and in the case of the alkali hydrides. The energies of the halide salts of Cu, Ag, Au, and Tl cannot however be accounted for on this basis. The bromides and iodides are certainly largely affected by other factors such as homopolar binding forces, the fluorides and chlorides to a smaller extent and

possibly not at all.

(5) The dipole moments of all the salts for which the calculated and experimental values of D_V agree are calculated.

Sec. 51, p. 1435 and p. 1528) discovered that an isotope of oxygen of mass 16 occurred to about 1 part in 1200 in ordinary oxygen, a curious discrepancy arose between the physical ratio of the weights of hydrogen and oxygen and the physical ratio determined by the mass spectroscope. These values had previously been in complete agreement (Proc. Roy. Soc. A, 111, p. 407, 1926). A possible explanation was that an isotope of oxygen existed in just sufficient abundance to bring the two results into harmony. In 1932 Urey, Mindes and Merz (Phys. Rev. 39, p. 1044) and Urey (Phys. Rev. 41, p. 1044) proved the existence of O^{16} as heavier than the study of the line spectra of hydrogen, which had been photographed at very high dispersion. The mass of this isotope, which is now usually called deuterium, or heavy hydrogen, was found to be 2.0146 (Cambridge, Phys. Rev., 41, p. 1044) or 2.0147 (Urey, Phys. Rev., 41, p. 1044) and was found to be ordinary hydrogen containing an approximately 1 part in 5000 (Urey and Guild, Phys. Rev., 41, p. 1044, 1933).

Since these two isotopes had a larger relative difference in mass than the isotopes of any other element, it was conceivable that they should be, at

INTRODUCTION

When, in 1929, Giauque and Johnson (J. A. Chem. Soc. 51, p. 1436 and p. 3528) discovered that an isotope of oxygen of mass 18 occurred to about 1 part in 1200 in ordinary oxygen, a serious discrepancy arose between the chemical ratio of the weights of hydrogen and oxygen and the physical ratio determined by the mass spectroscopy, these values having previously been in complete agreement (Aston, Proc. Roy. Soc. A, 115, p. 487, 1927). A possible explanation was that an isotope of hydrogen existed in just sufficient abundance to bring the two results into harmony. In 1932 Urey, Brickwedde and Murphy (Phys. Rev. 39, p. 164; 40, p. 1, 1932) definitely proved the existence of such an isotope from the study of the line spectrum of hydrogen, which had been photographed at very high dispersion. The mass of this isotope, which is now commonly called deuterium, or heavy hydrogen; was later determined to be 2.01309 (Bainbridge, Phys. Rev., 41, p. 396; 42, p. 1, 1932; 44, p. 57, 1933) and its abundance in ordinary hydrogen estimated at approximately 1 part in 5000 (Bleakney and Gould, Phys. Rev. 44, p. 265, 1933).

Since these two isotopes had a larger relative difference in mass than the isotopes of any other element, it was conceivable that they should be, of

all the elements, the easiest to separate.

Washburn and Urey (Proc. Nat. Acad. Sci. 18, p. 496, 1932) discovered that a fractionation of the isotopes occurred during the electrolysis of water. Lewis and Macdonald, who first prepared pure heavy water by this method (J. Chem. Physics, I, p. 341, 1933), found in the course of their experiments that the ratio of the rates of liberation of protium (or light hydrogen), H, and deuterium, D, was a constant α , given by the equation:-

$$d \log H = \alpha d \log D, \quad (1)$$

where α was independent of the isotopic ratio in the liquid and had an experimental value of about 5.

Another method by which a complete separation of the isotope was accomplished is due to Hertz (Z.f. Physik, 91, p. 810, 1934) who made use of a continuous many-stage diffusion process. Since this latter method cannot conveniently be operated on a large scale the former method is, at present, the one used in the commercial production of heavy water.

Experimental:

When work was commenced on this thesis the cheapest available source of heavy water of appreciable concentration was the Ohio Chemical Mfg. Co. which supplied 0.47% heavy water at £5 per gallon. Since about 400 cc. of about 2% concentration were required for the diffusion experiments to be described, three gallons of 0.47% concentration were bought and then concentrated to the desired extent by electrolysis.

The electrolysis was carried out in two stages: in the first stage were four cells and in the second one cell, all of 200-300 ccs. capacity. In the first stage nickel anodes and nickel cathodes were used, while in the second a platinum anode was substituted. Fig. I shows the design of cell used.

The electrolyte, NaOH, was always at least 4% by weight concentration. Since it was desirable that a current of about 10 amps. should be employed, the internal resistance of the cells was kept below 1.5 ohms. A higher resistance always resulted in overheating, the electrolyte boiling and frothing excessively. In order to save the liquid, in the case of a cell cracking, they were surrounded by jars containing paraffin or benzene from which the water was easily separated. These jars were in turn cooled by a stream of running water. The electrodes which were 10 sq. cm. in area were made as broad as possible, so that they did not become uncovered as the volume

of the solution was passed. A wide bell was placed over the cathode so that the gases were collected separately. In the second stage when it was necessary to prevent completely any mixture of the gases with the hydrogen evolved a similar setup was placed on the cathode.

Air condenser was used in the first stage in order to prevent any water vapour being carried over. In the second stage a CO_2 mixture was used to prevent any water vapour being carried over.

After the first stage the cathode was covered with a thin layer of oxide, while the anode was removed and cleaned with dilute sulphuric acid. The use of a second stage was necessary to prevent any water vapour being carried over.

Since the cathode would have been covered with oxide, it was necessary to attempt to remove it. The oxide was liberated from the second stage was, however, passed over CuO heated in a furnace at 500°C and the water produced passed on to a tray cooled at -80°C .

At the conclusion of each electrolysis the liquid from each stage was filtered, its volume noted and then distilled in the pyrex apparatus shown in Fig. 2.

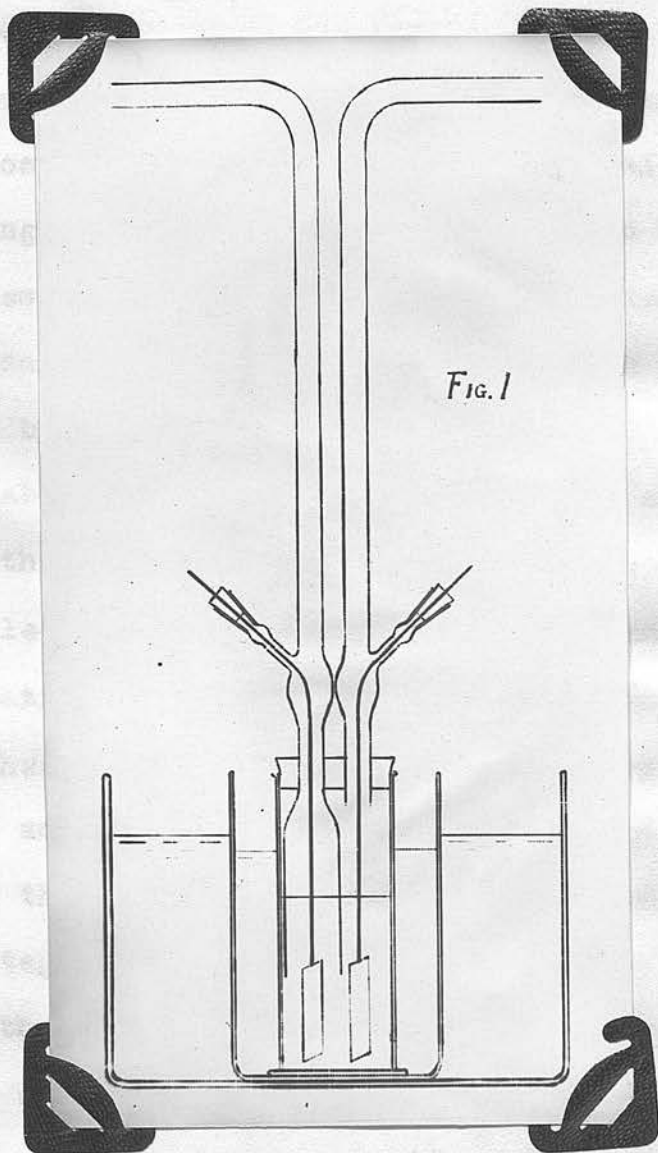


Fig. 1

of the solution was reduced. A wide bell was placed over the cathode so that the gases were collected separately. In the second stage when it was necessary to prevent completely any mixture of the oxygen with the hydrogen evolved a Soxhlet filter was placed on the cathode bell.

Air condensers 3 ft. long were found adequate to condense most of the water vapour, the remaining vapour being frozen out in traps surrounded by acetone- CO_2 mixtures. The bulbs shown on the condensers were necessary to break froth bubbles which were often carried up by the gases.

After about 30 hours' electrolysis the anode was covered with an adherent coating of a black nickel oxide, while the cathode was covered with an easily removed coating of nickel. The best method of cleaning these electrodes was found to be by abrasion. The use of acids was extremely pernicious since, when next used, the anode rapidly became oxidised and soon disintegrated.

Since the hydrogen liberated in the first stage would have a concentration of only about 0.1% D, no attempt was made to recover it. The hydrogen liberated from the second stage was, however, passed over CuO heated in a furnace at 500°C and the water produced frozen out in a trap cooled at -80°C .

At the conclusion of each electrolysis the liquid from each stage was filtered, its volume noted and then distilled in the pyrex apparatus shown in fig. 2.

The deuterium concentration of the liquids was determined by means of the interferometer (to be described later). 0.47% D_2O was now added to the electrolyte from stage 1, and the distillate from stage 1 added to the electrolyte from stage 2, the initial volumes measured and another electrolysis started.

From the concentration of the water at the beginning and the end of an electrolysis and the reduction in volume of the liquid the separation coefficient, α , is obtained by substitution in formula (2)

$$\frac{H_0}{H} \left(\frac{D}{D_0} \right)^\alpha = \left(\frac{V_0}{V} \right)^{\alpha-1}, \quad (2)$$

where H_0 and D_0 are the original and H and D the final concentrations of hydrogen and deuterium, and V_0 and V the original and final volumes. In all 15 electrolyses were made, in each case a little over 300 amp. hrs. being passed. The average value of α for the first stage was found to be 6.5 while for the second stage it was somewhat lower and averaged about 5.

Analysis:

In order to determine the deuterium content of small samples of heavy water, use was made of a Rayleigh Interferometer with which an analysis could be made using only 0.5 cc. of liquid. Although Luten (Phys. Rev. 45, p. 161, 1934) has shown that the refractive index of a heavy water solution decreases linearly with increasing deuterium content, this does not necessarily mean, as has been shown by Urey, Crist and Murphy (J. Chem. Phys. 2 p. 112, 1934), that the number of drum divisions on the screw controlling the compensating plate should be directly proportional to the deuterium concentration throughout a wide range. It is however evident from the latter author's paper that for concentrations up to about 3 mol.% any error introduced by assuming a linear relation between scale reading and deuterium content is less than the possible error of an observation. The instrument employed in this work was one of very high precision. It was possible to match its fringes to less than one fortieth of a fringe, that is, to set the drum scale to within .3 of a division.

In practice it was found possible to reproduce readings to ± 0.1 of a drum division when the total shift was less than 100 divisions. So precise a reading was not possible at exceedingly high readings of say 1000, due to the dispersion of the refracting solution being much greater than that of the

(1) 6.0 (2) 24.6 (3) 30.1

compensating plate. In this region the error could be as large as ± 1 drum division.

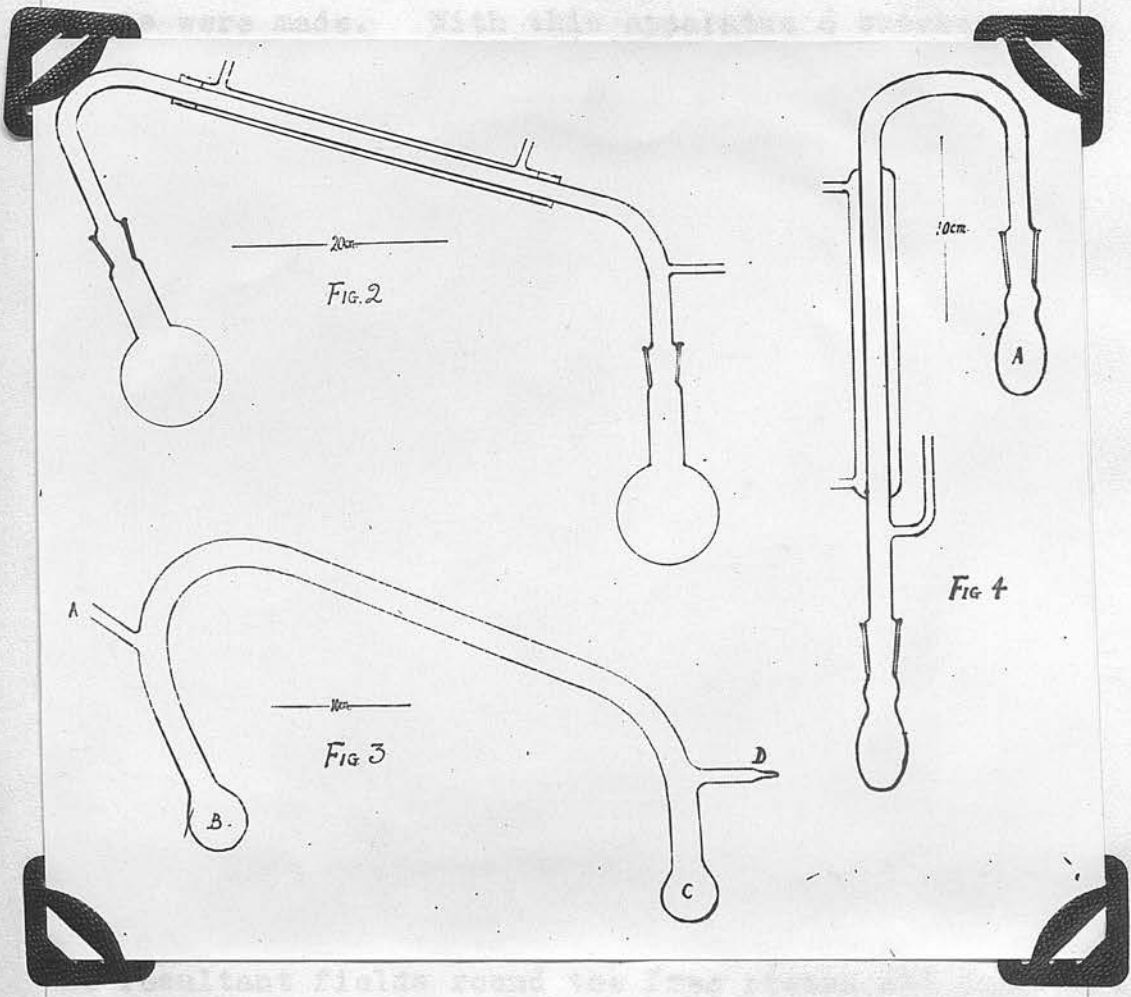
Before analysing a sample of water it was necessary that it should be rigorously purified. Where large volumes of liquid were concerned two or more distillations were made in the apparatus shown in fig. 2. Distillations of small quantities of liquid (1 or 2cc) were at first carried out in a pyrex apparatus such as that shown in fig. 3. The water was introduced by a small funnel at A and frozen in the bulb B by an ether-CO₂ mixture. A hyvac pump was connected to A and the apparatus evacuated for at least $\frac{1}{2}$ hr. The tube at A was then clipped, the freezing mixture transferred to bulb C and bulb B very gently warmed. The liquid was thus at once outgassed and distilled. When the distillation was complete, air was gradually let in at A, then the ice in C was melted, the nipple at D cut and the liquid run out into the interferometer cell.

This method had the disadvantage of being rather slow in operation. One observation of interest that may be mentioned is that it was quite simple to fractionate heavy water using this apparatus. In one experiment, for example, a sample of water giving an interferometer shift of 16.10 drum divisions was collected in three fractions which had the following readings

(1) 6.0 (2) 14.6 (3) 30.1

A communication by Fall and Jones in the J. Am. Chem. Soc. 56, p. 749, 1934. Some time after this had been noted here, confirms the observation.

An improved design of distillation apparatus which was used during the latter part of the work is shown in fig. 4. The apparatus was made of Pyrex glass. Three bulbs of type A with interchangeable



...sultant fluids round the free space and ... the force fields ... and ... bacterial ... species identical.

In the kinetic experiments which have ... the side and which involve the force fields ... it has been found that there is no

A communication by Hall and Jones in the J. Am. Chem. Soc. 56, p. 749, 1934, some time after this had been noted here, confirms the observation.

An improved design of distillation apparatus which was used during the latter part of the work is shown in fig. 4. The apparatus was made of pyrex glass. Three bulbs of type A with interchangeable joints were made. With this apparatus 6 successive distillations could be made in $\frac{1}{2}$ hour, thus ensuring a thorough outgassing and complete purification of the liquid.

Rate of Diffusion of HDO in H₂O.

Possibly the property of heavy hydrogen most important to chemists will be its use as an isotopic indicator. The distinction between protium and deuterium lies almost solely in the constitution of the nuclei, which have different masses but the same atomic number and the same electronic charge. Although a slight difference apparently (Pollard and Margenau, Nature 135, p. 393, 1935) does exist between the resultant fields round the free proton and the deuteron, the force fields round a protium and round a deuterium compound must be for all practical purposes identical.

In the kinetic measurements which have so far been made and which involve the force fields around molecules it has been found that there is no

difference in behaviour when a deuterium compound is substituted for an ordinary hydrogen one. (Melville Nature 133, p. 947, 1934). However in measurements where a hydrogen linkage is broken or formed a definite difference in behaviour is obtained. This difference is due to the fact that every chemical bond has a fundamental vibration frequency ν_0 , which is associated with an energy = $\frac{1}{2} h\nu_0$.

$$\text{and } \nu_0 = \frac{1}{2\pi} \sqrt{\frac{f}{M}} \text{ sec}^{-1},$$

where f (dynes/cm) is the restoring force per unit displacement and is the same for deuterium and protium compounds;

where M is the reduced mass of the oscillator A-B and is equal to $\frac{M_A M_B}{M_A + M_B}$, where M_A and M_B are the atomic weights of A and B; and

where h is Planck's constant (6.55×10^{-27} erg-secs.)

Hence it is evident that the mass of the atoms is involved in the zero-point energy, which in turn modifies the activation energy of a reaction and thus a difference in reaction rate will occur for different isotopes.

Thus one can determine whether a process involves free atoms or ions, or whether molecules only are involved, for in the first case, a difference in behaviour will result when deuterium is substituted for protium, while in the second case, no difference will result.

Another obvious way in which heavy hydrogen will

function as an indicator in chemical reactions is, by using it to 'label' certain hydrogen atoms in a reacting mixture, subsequent analysis being made to determine how the labelled hydrogen atoms have reacted.

The diffusion experiments to be described are an example of the application of the last-mentioned use of deuterium as an indicator.

1. The apparatus in this case consisted of 4 cylindrical tubes; two 14.2 cm. long, one being .9 cm. in diameter and the other .6 cm.; and two 9.4 cm. long, one being .85 cm. in diameter and the other .6 cm.

These were filled with the liquid whose diffusion rate was required and held rigidly upright in glass stands, which were then placed in a bath through which wash liquid flowed extremely slowly (see fig. 5).

Some experiments were carried out initially with KNO_3 in the tubes to determine the best conditions for starting and finishing an experiment and also to determine the rate of flow of wash liquid permissible.

It was found that rates of flow up to 200 cc. per hour were allowable, and that when the liquid rose to the tops of the diffusion tubes, sharply defined interfaces of separation were obtained. Similarly, if the liquid was run out at the same rate at the end of an experiment no noticeable mixing occurred at the

Experimental:

As may be judged from the variety of values given in the I.C.T., the rates of diffusion of simple molecules are very difficult quantities to measure accurately. Besides this, different experimental methods apparently often yield widely varying figures.

In the following experiments two methods were tried, I, that which may be described as the cylindrical tube method and II, Northrup and Anson's sintered glass plate method.

I. The apparatus in this case consisted of 4 cylindrical tubes; two 14.2 cm. long, one being .9cm. in diameter and the other .6 cm; and two 9.4 cms long, one being .85 cm. in diameter and the other .6 cm.

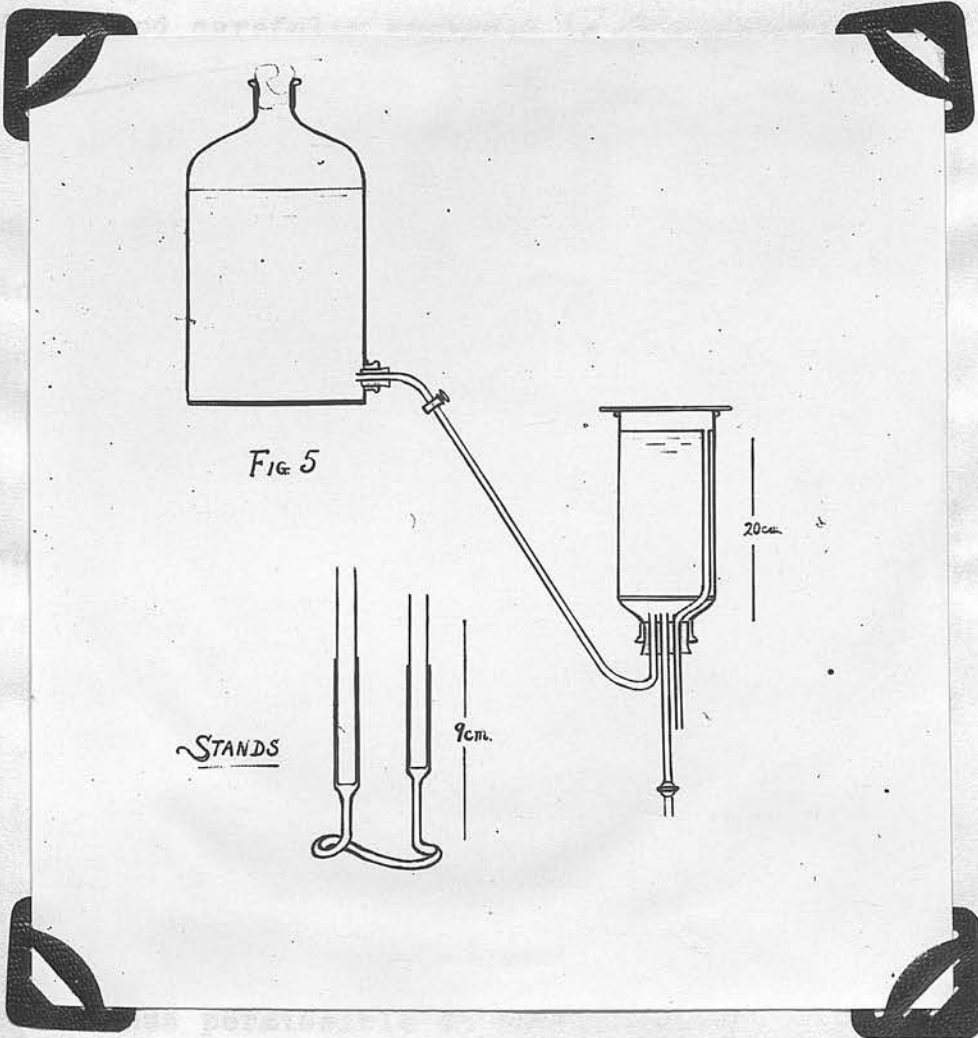
These were filled with the liquid whose diffusion rate was required and held rigidly upright in glass stands, which were then placed in a bath through which wash liquid flowed extremely slowly (see fig.5).

Some experiments were carried out initially with KMnO_4 in the tubes to determine the best conditions for starting and finishing an experiment and also to determine the rate of flow of wash liquid permissible.

It was found that rates of flow up to 200 cc. per hour were allowable, and that when the liquid rose to the tops of the diffusion tubes, sharply defined interfaces of separation were obtained. Similarly, if the liquid was run out at the same rate at the end of an experiment no noticeable mixing occurred at the

mouth of the tubes. The apparatus was extremely sensitive to vibration and was held rigid as on a solid base as previously. In order to maintain a constant temperature these experiments were done at the constant temperature bath of the laboratory.

A stock of 250 cc. of aqueous solution of sodium chloride was obtained from the electrolysis of sodium chloride.



The readings for η and η_{sp}/c were taken at intervals of 15 minutes. During the longest of these runs, the concentration of an experiment, given in Table I, was 0.01 g./100 cc. of water. The diffusion coefficient D is given in Table I.

mouths of the tubes. The apparatus was, however, extremely sensitive to vibration and was thus placed on as solid a base as possible. In order to preserve a constant temperature these experiments were done in the constant temperature room at $(14 \pm .05)^\circ \text{C}$.

A stock of 250 cc. of approximately $1\frac{1}{2}$ mol.% D_2O , obtained from the electrolysis was distilled three times and carefully analysed in the interferometer before being placed in the diffusion tubes. Pure distilled water was used for the wash liquid. After an experiment the liquid in the tubes was transferred to clean dry bottles and subsequently distilled and analysed.

In these analyses the drum reading is proportional to the mol. fraction of heavy water in the sample, while in formula (1) below volume concentrations are required. However, since the molecular volumes of pure heavy water (viz. 18.126 cm.) and ordinary water (viz. 18.060 cm.) differ by less than 0.4% no significant error is introduced by assuming that the concentration expressed as a mol. fraction is directly proportional to the concentration in volume units. It is thus permissible to substitute the appropriate drum readings for V_0 and V in the fraction $(\frac{V_0 - V}{V_0})$ of equation (1).

Knowing the length of tube used, h (cms), the duration of an experiment, t (secs.), and the initial and final concentrations V_0 and V of D_2O in the tube, the diffusion coefficient D is then given by:

$$D = - \frac{4h^2}{t\pi^2} \log_e \left\{ 1 - \frac{V_0 - V}{V_0} \cdot \left(\frac{\pi^2}{8} \right) \right\} \text{ cm}^2/\text{sec.} \quad (1)$$

The results for the diffusion of pure water are given in Table 1.

Experiments were also carried out using .011N NaOH of $1\frac{1}{2}\%$ D concentration, 5 litres of wash liquid of exactly the same alkaline concentration being used.

The values obtained are given in Table 2.

Table 2

Length of tube (cm)	Time of expt. (secs)	Initial Drum reading	Final Drum reading
14.2(a)	91230		
9.4(a)	9.520	13.95	
14.2(a)	207870		
14.2(b)	207840	16.4	
9.4(c)	207730		

(a) diam. of tube = 3.8 cm
 (b) " " " " " " " "
 (c) " " " " " " " "

Table I.

Length of tube (cm)	Time of expt. (secs)	Initial Drum reading	Final Drum reading	$D \times 10^5$ $\text{cm}^2/\text{sec.}$
14.3	82005	33.0	26.65	21.6
7.1	81495		11.0	27.6
14.2(a)	46965	16.95	15.5	19.4
14.2(b)	47460		15.3	22.3
9.4(c)	47010		14.5	14.9
9.4(b)	47325		14.5	14.9
14.2(a)	86202	18.35	17.05	8.66
14.2(b)	86280		16.45	12.9
9.4(c)	86574		15.45	8.97
9.4(b)	86520		14.5	12.4

Table II.

Length of tube (cm)	Time of expt. (secs)	Initial Drum reading	Final Drum reading	$D \times 10^5$ $\text{cm}^2/\text{sec.}$
14.2(a)	91230	13.95	11.85	18.2
9.4(a)	9.320		9.55	19.3
14.2(a)	207870	18.4	15.35	11.3
14.2(b)	207840		15.15	12.2
9.4(c)	207720		7.25	23.8

(a) diam. of tube = .9 cm.

(b) " " = .6 cm.

(c) " " = .85 cm.

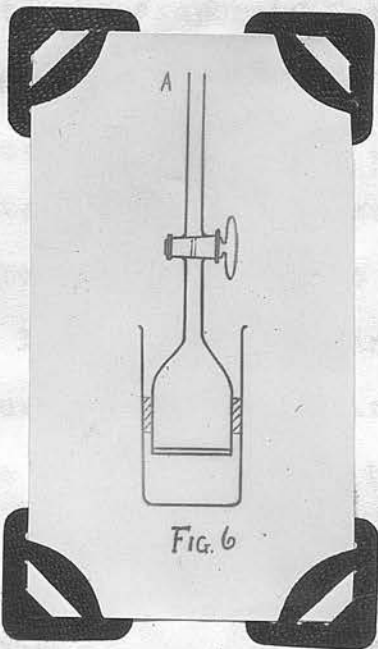
II. Northrup and Anson's Method (J. Gen. Physiol., 12 p. 543, 1929).

This method which has been experimentally tested by McBain and Liu (J. Am. Chem. Soc. 53, p. 59, 1931) is one capable of giving diffusion coefficients with an accuracy and reproducibility greatly in advance of any other method. The apparatus, which is shown in figure 6, consists of a bell-shaped sintered glass filter (specified technically as G4), which is closed at the top by a stopcock A. The bell carries a rubber ring so that it fits tightly into a beaker as shown. In the experiments to be described two such pieces of apparatus were obtained, the volumes of the cells being 24.0 cc. and 23.4 cc. and the beakers 100 cc.

The experimental procedure employed followed closely that described by McBain (loc.cit).

The cell was first of all washed several times with chromic acid solution by drawing up through the pores with a filter pump and then expressing under pressure. The cell was then washed at least 10 times and steeped for some hours in distilled water. In order to remove air from the pores air-free distilled water was drawn into the cell by reducing the pressure at A by 15 cm. Just before it was filled the pressure was suddenly increased so that all the air was finally dislodged from the pores.

The water was then filtered through a filter paper of
pressure of 1 meter of water. The filtered water was
filter dust from the apparatus. The water was then
a sintered glass filter. The water was evaporated
until the last layer was dried. The water was
The cell was then placed in a desiccator and the
through the diaphragm and the water was evaporated
bubbles to the surface. The water was evaporated



the surface of the water. The water was evaporated
the cell was now placed in a desiccator and the
given temperature. The water was evaporated
diffusion cell. The water was evaporated
depending on the rate of evaporation. The water was
the apparatus. The water was evaporated

after removing the apparatus from the desiccator and
cell was now transferred to a glass beaker containing
a volume of gas-free water equal to the volume of
solution in the cell, and the diffusion experiment
proper began.

After sufficient time had elapsed to permit
of an accurate analysis of the solution in the beaker
the cell was removed, rinsed with filter paper, and
the solution in the cell extracted through the diaphragm.
The first 5 cc. or so was discarded and the

The water was then driven out of the cell with a pressure of 1 metre of water, care being taken to filter dust from the air stream by passing it through a sintered glass filter. The liquid was expressed until the last layer was about to enter the pores. The cell was then rinsed and charged with the solution through the diaphragm and filled completely without bubbles to the stopcock, which was then closed. Liquid adhering to the diaphragm was removed by touching with a glass rod and the cell then placed in position (see fig. 6) in the beaker, the diaphragm being set accurately horizontally and immersed in the surface of about 24 cc. of pure gas-free water. The cell was now left for preliminary diffusion at a given temperature, the time required for steady diffusion columns to be set up in the glass pores depending on the solution used. 2-2½ hours were given in the experiments to be described here.

After removing the adherent liquid as before the cell was now transferred to a clean beaker containing a volume of gas-free water equal to the volume of solution in the cell, and the diffusion experiment proper begun.

After sufficient diffusion had occurred to permit of an accurate analysis of the solution in the beaker the cell was removed, wiped with filter paper, and the solution in the cell extruded through the diaphragm, the first 5 cc. or so being discarded and the

remainder reserved for analysis.

Since it was very important that the diaphragm of the cell be accurately horizontal during the diffusion, the level was carefully adjusted while being observed by a Casella cathetometer, through which it was quite easy to detect any deviation from the horizontal.

All the distilled liquids used in connection with this work were freed from air by shaking them vigorously in the vacuum produced by a good water pump. The standard solutions of KCl were also made up using outgassed water.

Calculation: From Fick's equation the amount of a substance ds diffusing per interval of time dt is

$$ds = DA \frac{dc}{dx} dt,$$

where D is the diffusion coefficient of the substance, C its concentration and A the effective area of all the pores in the diaphragm.

Now within the disc which has a uniform width dx , there is a linear change in concentration between the concentration in the cell above and the solution below; hence $\frac{dc}{dx}$ may be replaced by $\frac{\Delta c}{\Delta x}$

Here it should be noted that the solutions above and below the diaphragm are perfectly homogeneous and that mixing is complete (McBain and Liu loc.cit.)

Since the volume of water V in the beaker is equal to that in the cell then,



$$\frac{ds}{dt} = D \left(\frac{A}{\Delta x} \right) (c_0 - 2c),$$

where c_0 is the initial concentration, and $c = S/V$, the concentration to which the solution in the beaker has attained, 'S' being the amount of substance having crossed the diaphragm;

Hence

$$\frac{ds}{dt} = \frac{1}{V} \cdot \frac{dc}{dt} = D k' (c_0 - 2c)$$

$$k' = \left(\frac{A}{\Delta x} \right)$$

$$\text{i.e. } \frac{dc}{dt} = D k'' (c_0 - 2c)$$

$$k'' = k' V$$

$$\therefore \log(c_0 - 2c) = -2Dk''t + \alpha$$

$$\text{but } \alpha = \log c_0 \quad (t=0)$$

$$\therefore DC = \frac{\log_{10} c_0 - \log_{10} (c_0 - 2c)}{t},$$

where C is the cell constant and t is the time of an experiment.

The cell constant C is determined with reference to a substance whose diffusivity is known. In this case $1.448 \text{ cm}^2/\text{day}$ is taken as the coefficient of diffusion of .1N KCl into water at 20°C .

Since, in the actual experiment, the concentration of the solution put into the cell is altered slightly by the liquid in the diaphragm, the true initial concentration is given by $c + c'$, where c is the final concentration in the cell and c' the final concentration in the beaker.

$$\text{Then } c - 2c = c + c' - 2c' = c - c'$$

and finally the equation employed is :

$$D = \frac{\log_{10} \frac{c + c'}{c - c'}}{C \times t} \quad (2)$$

In order to perform the experiment at 20°C the cells (fig. 6) were lowered into tall cylindrical jars which were immersed in a thermostat at 20°C.

The solutions of KCl were analyzed by means of the interferometer which was first calibrated from solutions of known concentration (see graph I.).

The KCl used had been purified by recrystallization, for conductivity work. Before being used it was heated to dull redness in a covered crucible for 4 hours and then cooled in a desiccator.

Determination of the Cell Constants C:

In order to perform the experiment at 20°C the cells (fig. 6) were lowered into tall cylindrical jars which were immersed in a thermostat at $20 \pm .01^{\circ}\text{C}$.

The solutions of KCl were analysed by means of the interferometer which was first calibrated from solutions of known concentration (see graph I.)

The KCl used had been purified by recrystallisation, for conductivity work. Before being used it was heated to dull redness in a covered crucible for $\frac{1}{2}$ hour and then cooled in a desiccator.

Expt.		Time (mins)	No. of drum divisions	Normality of KCl	C	Average value of C
I	Cell I	1281	235.1	.0895	.0559	.0541
	Beaker I		20.0	.0074		
II	Cell I	1396	241.2	.0913	.0523	
	Beaker I		20.3	.0077		
I	Cell II	1213	241.9	.0842	.092	.0903
	Beaker II		30.8	.0117		
II	Cell II	1381	247	.0861	.0855	
	Beaker II		32.95	.0121		

Results.(a) Calibration of the Interferometer.

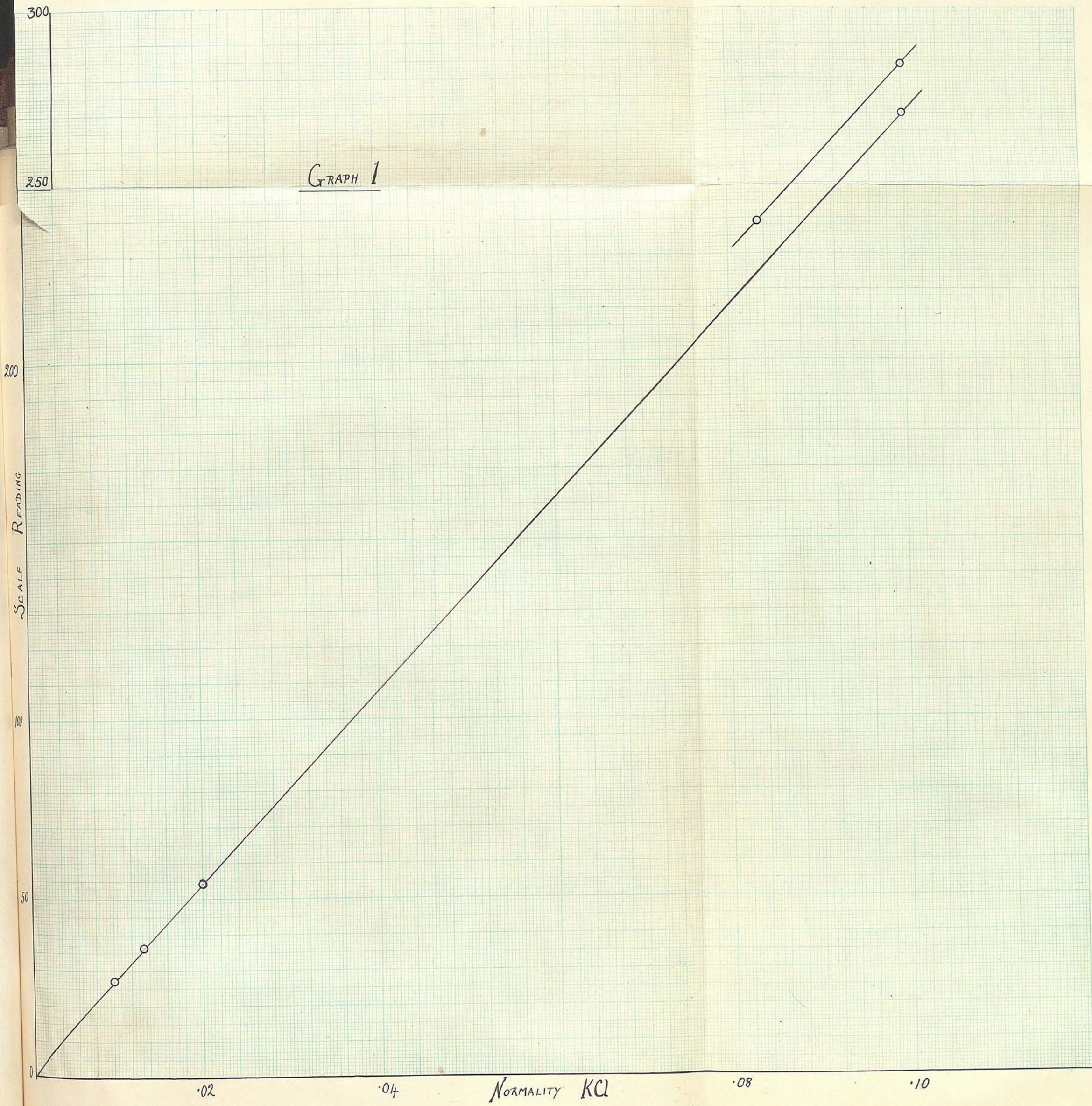
Normality KCl	0.1	.0833	.02	.0133	.01
Reading	284.1	239.0	54.2	36.2(5)	27.0(5)

The reading for one fringe lower than the most distinct at 0.1N (viz. 270.0) falls accurately on the linear extrapolation of the line through the first three points. (See graph I.)

(b) Cell Constants.

Expt.		Time (mins)	No. of drum divisions.	Normality of KCl	C	Average value of C
I	Cell I	1281	256.1	.0895	.0559	.0541
	Beaker I		20.0	.0074		
II	Cell I	1396	261.2	.0913	.0523	
	Beaker I		20.9	.0077		
I	Cell II	1213	241.9	.0842	.092	.0903
	Beaker II		30.8	.0117		
II	Cell II	1381	247	.0861	.0885	
	Beaker II		32.95	.0121		

GRAPH 1



Analysis:

In these experiments density measurements were used in place of the interferometer method, to analyse samples of heavy water.

The densities of ordinary and heavy water at 25° C are .99706 and 1.10486 respectively according to Lewis and Macdonald (J. Am. Chem. Soc. 55, p.3057, 1933). The difference in density at 25° is therefore 0.1078.

If now M_1 and M_2 are the weights of a pycnometer filled with heavy and with ordinary water respectively, and, if the actual weight of ordinary water in the pycnometer is M , then the difference in density $\Delta\rho$ is,

$$\Delta\rho = \frac{1}{V} (M_1 - M_2) \quad (V = \text{volume of pycnometer})$$

and since the densities of pure D_2O and H_2O differ by .1078, the mol.% D_2O in a sample is,

$$\frac{100 \Delta\rho}{.1078} = \frac{100 \times .99706}{.1078 \times M} (M_1 - M_2) \quad (3)$$

All the weighings were done with accurately calibrated weights and were repeated until values agreeing to 0.1 milligram were obtained.

The pycnometer was of a U-shaped design as shown in fig. 7(a) and had a capacity of about 14 cc. The levels were adjusted to marks on the capillary necks while the pycnometer was immersed in a thermostat controlled to within +.002 of 25° C.

This design of pycnometer is quite easy to set

perfectly accurately; it is however easily dried
and polished before being inserted by the glass
stirrup (fig. 7(b)) in the battery.

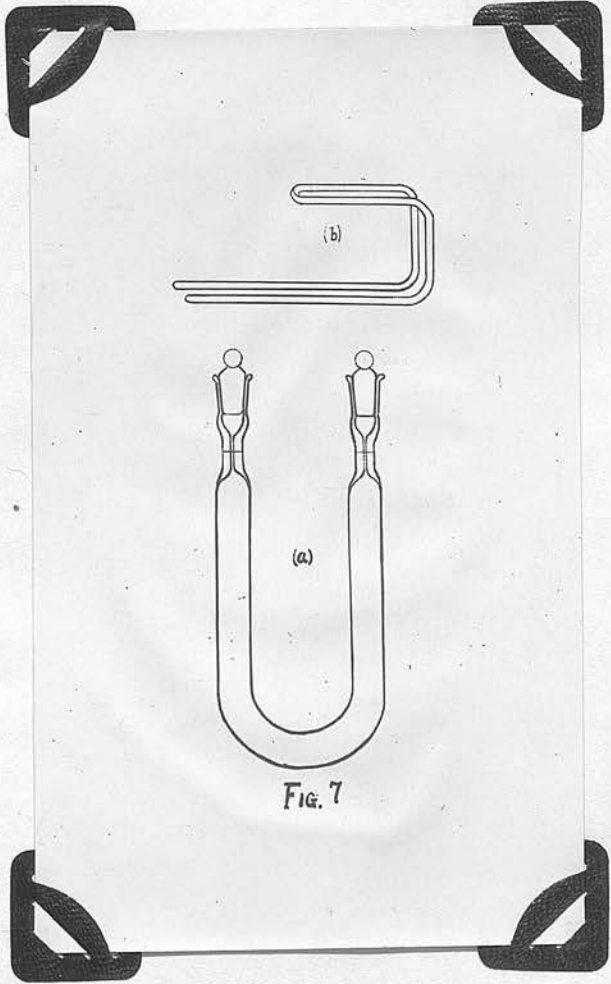


FIG. 7

perfectly accurately: it is moreover easily dried and polished before being suspended by the glass stirrup (fig. 7(b)) in the balance.

shown by the following results.

Mass of pycnometer with ordinary paper

Mass of pycnometer

Mass of ordinary paper in pycnometer

Mass of pycnometer with heavy paper

Hence from equation (1) the apparent density

$$\frac{100 + 9.000}{107.000} = \dots$$

In the diffusion formula (2) the concentration is the ratio $\frac{C_1 - C_2}{C}$ and it is not very far from unity as is already shown however, for heavy paper and fractions, or quantities measured, and for the need. The mol. fraction of a gas in a mixture of measurements is proportional to the appropriate values of the diffusion coefficient for values of g .

The data necessary for

is Table III. The values of

are in thermostat with

constant temperature

Diffusion experiments were made

presence of H_2O and of H_2

1 normal. The values of

Results:

The heavy water initially used in these experiments had a deuterium concentration of 1.80 mols.% as shown by the following results.

Mass of pycnometer with ordinary water (M_2) = 49.0450 grms.

Mass of pycnometer = 35.3486 "

.. Mass of ordinary water in pycnometer (M) = 13.6964 "

Mass of pycnometer with heavy water (M_1) = 49.0717 "

Hence from equation 3 the concentration is,

$$\frac{100 \times 99706}{1078 \times 13.6964} (49.0717 - 49.0450) = 1.80 \text{ mol\% D}_2\text{O}$$

In the diffusion formula (2) the concentrations in the ratio $\frac{C+C'}{C-C'}$ are to be expressed in volume units. As already shown however, for heavy water, mol. fractions, or quantities proportional to these may be used. The mol. fraction of a sample in these density measurements is proportional to ($M_1 - M_2$) so that the appropriate values of this quantity may be substituted for values of c .

The data necessary for calculating D are collected in Table III. The experiments at 23° and 0.1° were done in thermostats while that at 14.3° was done in a constant temperature room.

Diffusion experiments were also carried out in the presence of H_2SO_4 and of Na_2SO_4 at concentrations of 1 Normal. The solutions of H_2SO_4 (and Na_2SO_4) in

the heavy water for the cell and the ordinary water for the beaker were made up volumetrically. Before an analysis could be made the H_2SO_4 (and Na_2SO_4) had to be removed from the liquid. In the case of Na_2SO_4 four simple distillations in the apparatus shown in fig. 4 sufficed. The bulk of the H_2SO_4 was neutralised with freshly burnt CaO , excess $CaCO_3$ then added and the liquids distilled 4 or 5 times.

The results for these experiments which were done in a constant temperature room are given in Tables IV and V.

Cell I	240	
Beaker I	22	1.05
Cell II	232	
Beaker II	28	1.05
Cell I	224	
Beaker I	28	1.33
Cell II	205	
Beaker II	40	1.22

Table III.

Temp. °C		Time mins.	No. of milligrms x 10	D x 10 ⁵ x cm ² /sec.	Average D.
25 ± .002	Cell I	1429	234	2.49	2.52
	Beaker I		31		
	Cell II	1207	223	2.55	
	Beaker II		42		
14.3 ± .02	Cell I	1320	240	1.86	1.80
	Beaker I		22		
	Cell II	11.40	232	1.75	
	Beaker II		28		
0.1 ± .1	Cell I	2517	224	1.335	1.39
	Beaker I		28		
	Cell II	2537	205	1.44	
	Beaker II		46		

Table IV. NH_2SO_4

Temp. °C		Time mins.	No. of Milligrms x 10	$D^5 \times 10^5$ $\text{cm}^2/\text{sec.}$	Average D
13.5 ± .05	Cell I	1342	210	1.71	1.70
	Beaker I		18		
	Cell II	1180	202	1.69	
	Beaker II		25		

Table V. $\text{N.Na}_2\text{SO}_4$

Temp. °C		Time mins.	No. of Milligrams x 10	$D \times 10^5 \times$ $\text{cm}^2/\text{sec.}$	Average D
13.85 ± .05	Cell II	1360	186	1.63	1.66
	Beaker II		25		
	Cell II	1353	177	1.69	
	Beaker II		25		

Discussion.

The difference in mass of heavy and light water accounts directly, or indirectly, for the significant differences which exist in their physical properties. Difference in molar refractivity is due to difference in the fundamental vibration frequencies of bonds involving hydrogen; differences in specific heat, boiling and freezing points and in the "structure" of the liquids (in Bernal and Fowler's sense, J. Chem. Physics, 1, p.515, 1933) are due to differences in energy-distribution among the molecules; and both the fundamental frequency and energy-distribution involve mass.

Differences in viscosity may depend chiefly on the difference of the liquid "structures"

It is however probable that the van der Waals and dipole forces around the two isotopic forms of water are identical.

In the experiments described with 1-2% heavy water the liquid must have essentially a light water structure. Were the 2% D-atoms merely "labels", then the experiments would give the rate of self-diffusion of water molecules. However the extra mass of the D-molecules will presumably lower the rate of diffusion of these relative to ordinary water molecules and so the figures obtained will differ from the rate of self-diffusion of water to some extent, but by not more than 2%.

In the experiments by Method II this is within the experimental error.

Considering the results in general, it is evident that the earlier experiments using Method I definitely give a very erroneous value to D . The failure is possibly due to the fact that large disturbances take place at the exits of the tubes. The very small difference in density, (0.2%), between the solutions and wash liquid would render the experiment extremely sensitive to slight temperature variation and slight mechanical vibration.

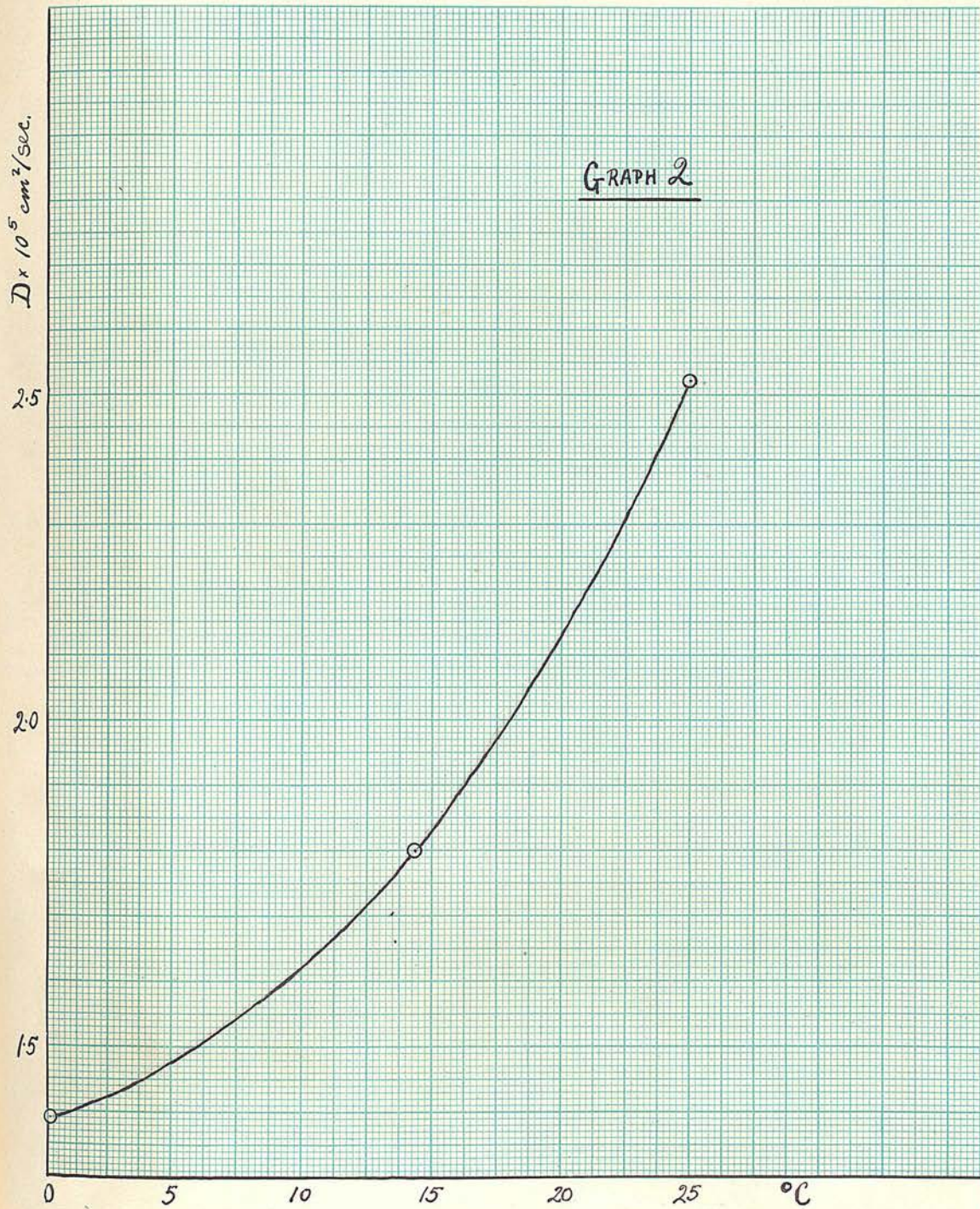
The results obtained from Method 2 (table 3) are concordant, reproducible and, moreover, are in harmony with the values of the molecular diffusion of similar light molecules, such as formic acid and formaldehyde. The accuracy of the results is very sensitive to the value obtained for the final concentration of heavy water in the beaker. For example an error of 0.1 milligrams in the weighing gives rise to an error of about 6% in the value of D . An error of 5% is also inherent in the experimental method itself. Thus although an error of 11% may occur in individual results the average values obtained should be accurate to 6%. The variation of D with temperature is given on graph 2.

Einstein (Z.f. Electrochem., 14, p.235, 1908) has derived a theoretical expression for D in terms of the viscosity, η , of the liquid medium and the

radius, r_0 , of the diffusing molecules is:

$$D = \frac{kT}{4\pi r_0^2 \eta}$$

This equation was derived for the case in which



units.

This value is in fair agreement with that

calculated by Debye and Hückel (see eq. 1), namely

radius, r , of the diffusing molecules viz.

$$D = \frac{RT}{N} \frac{1}{6\pi\eta r}$$

This equation was derived for the case in which the diffusing molecules are large compared to the molecules of the solvent. If it holds for the present experiments the quantity $D\eta/T$ should be constant.

Temp. °C	$\eta \times 10^3$ c.g.s.	$D \times 10^5$ c.g.s.	$D\eta/T$
0.1	17.86	1.39	.091
14.3	11.65	1.80	.073
25.0	8.949	2.52	.076

The values of $D\eta/T$ at 14.3 and 25.0 °C. in the above table are constant (within the experimental error), while the value at 0.1 diverges by 20%. It is possible that the structural conditions existing at 0 °C. in liquid water would vitiate the conditions under which the above equation applies.

A further test of the equation is to employ it to calculate r , the radius of the water molecule.

Rearranging we have,

$$r = \left(\frac{RT}{6\pi N} \right) \frac{1}{\eta D}$$

$$\text{i.e. } r = 7.273 \frac{RT}{\eta D} \times 10^{-18} \text{ cm.}$$

At 18 °C. $D = 2.0 \times 10^{-5}$ cm²/sec and $\eta = 10.60 \times 10^{-3}$ c.g.s. units. Hence, $r = 1.00 \times 10^{-8}$ cm.

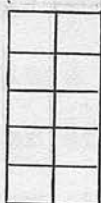
This value is in fair agreement with that calculated by Bernal and Fowler (loc.cit.), namely

$r_{-} = 1.38 \times 10^{-8}$ cm, and would indicate that the Einstein equation applies with considerable accuracy to the interdiffusion of small molecules.

An estimate of the rate at which molecular interchanges take place in a liquid can be obtained from the following calculation.

Consider a plane face of unit area composed of D_2O molecules placed in contact with a similar plane of H_2O molecules as shown in Fig. 8.

fig 8



Since the atomic volumes of H_2O and D_2O molecules are very nearly equal (see page 46) the number of molecules in each unit plane will be the same, and equal to,

$$\left(\frac{6.06 \times 10^{23}}{18.07} \right)^{2/3} = 1.04 \times 10^{15},$$

where 18.07 cc. is the atomic volume of the water molecules and 6.06×10^{23} is Avogadro's number.

Now the gradient, $\frac{dc}{dx}$ occurring in Fick's equation,

$$ds = DA \cdot \frac{dc}{dx} \cdot dt$$

is in this case = $\left(\frac{6.06 \times 10^{23}}{18.07} \right)^{4/3},$

$$\text{where } dc = \frac{6.06 \times 10^{23}}{18.07} \quad \text{and } dx = \left(\frac{18.07}{6.06 \times 10^{23}} \right)^{1/3}$$

Hence since $A = 1$ and $D = 2.0 \times 10^{-5}$ cm²/sec. at 18 °C, the number of molecules which interchange per second

$$\begin{aligned} \text{is } \frac{ds}{dt} &= 2 \times 10^{-5} \left(\frac{6.06 \times 10^{23}}{18.07} \right)^{4/3} \\ &= 2.16 \times 10^{25} \end{aligned}$$

The average life of a molecule in the layer is thus

$$\frac{1.04 \times 10^{15}}{2.16 \times 10^{25}} \approx 5 \times 10^{-11} \text{ sec.}$$

It is interesting to consider the meaning of this figure. The molecules in a liquid may be supposed to be vibrating about mean positions. Occasionally one molecule acquires sufficient energy to escape from its territory. If the vibrational frequency is known, it is possible to calculate roughly in what fraction of the total number of vibrations, a molecule "escapes". The vibrational frequencies in liquid water, as determined from infra-red and Raman spectra, are of the order of 3400 cm^{-1} , i.e. $1.08 \times 10^{14} \text{ sec}^{-1}$ (Rank, J. Chem. Physics, 2, p. 464, 1934). The "escape frequency", which is the inverse of the average life of a molecule, is $2 \times 10^{10} \text{ sec}^{-1}$ and therefore one "escape" takes place in $\frac{1.08 \times 10^{14}}{2 \times 10^{10}} (\approx 5000)$ vibrations.

We can now estimate the vibrational energy which is required to effect an "escape".

For, if N_0 is the number of molecules in the lowest vibrational level, E_0 , and N is the number having a vibrational energy, E , then

$$\frac{N_0}{N} = e^{-\frac{E-E_0}{RT}}$$

Substituting the value 5000 for N_0/N in this equation, we obtain $E - E_0 = 4900 \text{ cal.}$

Thus we arrive at a rough estimate of 5000 cal., as the activation energy required for diffusion.

Another estimate of the same quantity may be

obtained from the temperature coefficient of the diffusion coefficient. If we write tentatively

$$\frac{d \log D}{dT} = \frac{\Delta E}{RT^2}$$

ΔE may be regarded as the activation energy for diffusion. When $\log D$ is plotted against $1/T$ a straight line is not obtained (see graph 3). This would indicate that the activation of the diffusion process is not a simple quantity, as might perhaps be expected with a complex liquid like water, where the nature of the linkage between molecules varies with the temperature. However the value of ΔE for 0-15° C is 2850 and for 15 - 25° C., 5390 cal; and these quantities are certainly of the same order of magnitude as that calculated above.

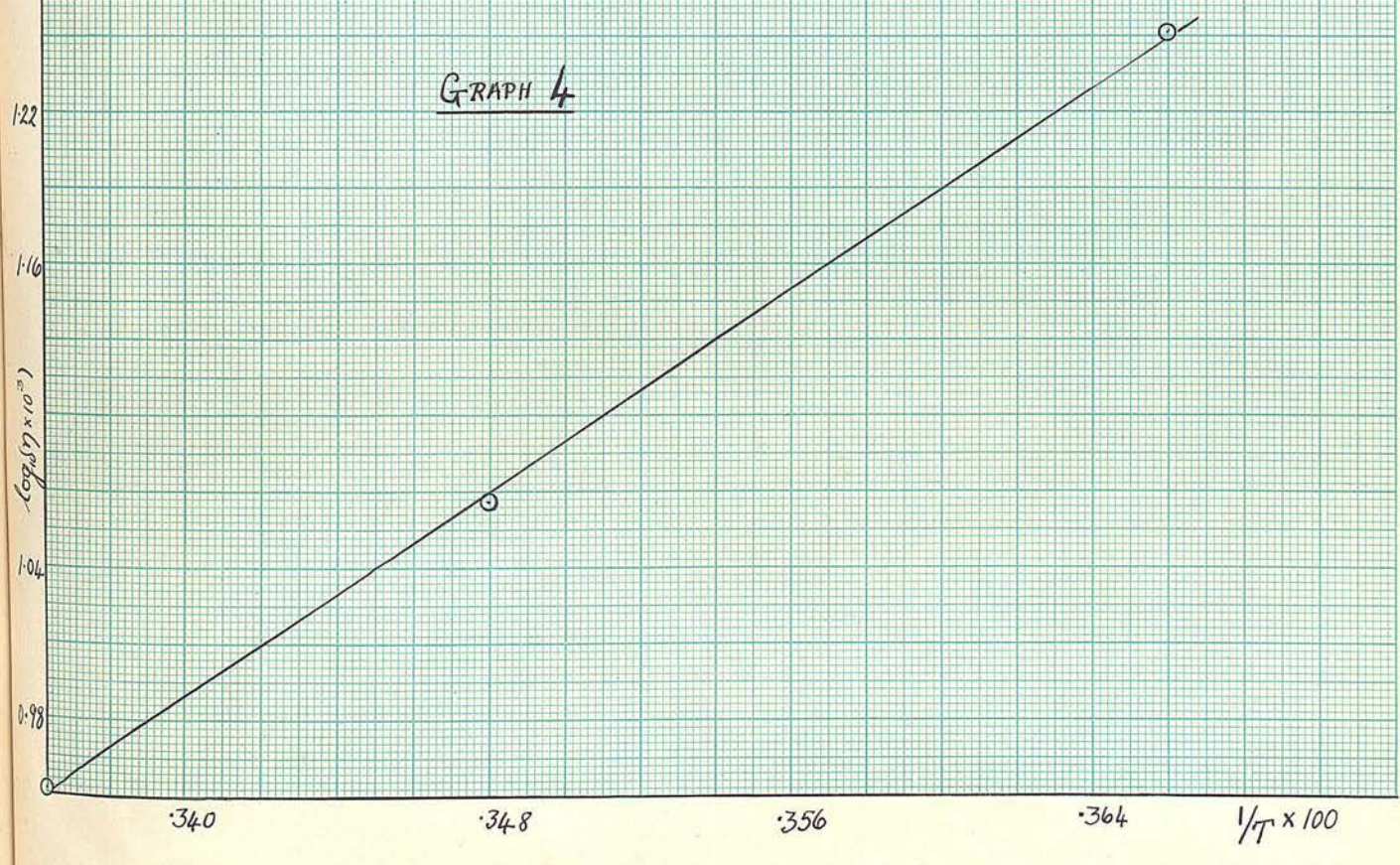
It may perhaps be significant that, from the temperature coefficient of the viscosity of water over the same range (see graph 4), we obtain from the equation,

$$\frac{d \log \eta}{dT} = \frac{\Delta E'}{RT^2}$$

the value $\Delta E' = 5000$ cal.

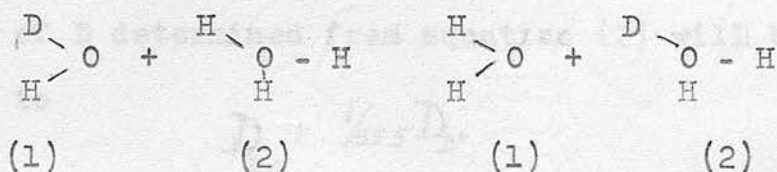
This agreement is indicative of the close connection which exists between the nature of viscosity and diffusion.

The exceptionally high values of D obtained originally by Method I could not possibly have been due to molecular motion, so it was thought that some kind of quantum diffusion of hydrogen took place,



possibly via hydrogen or hydroxyl ions. If such an effect occurred it should be greatly enhanced by the addition of $(\text{OH}_3)^+$ ion and $(\text{OH})^-$ ion to the diffusing liquid. The results listed in table 2, which were obtained in the presence of $(\text{OH})^-$ ion do not differ significantly however from those in table I.

The effect was also investigated by Method 2, in this case, in the presence of H_2SO_4 . If the presence of $(\text{OH}_3)^+$ in ordinary water facilitated a change of the following kind, in which atoms diffuse by quantised jumps, then the effect of increasing the concentration of $(\text{OH}_3)^+$ would be to increase the rate of the reaction,



enormously. No such increase in D was however found as may be seen from table 5.

A slight increase is however to be expected from the diffusion of the deuterium ions. The natural rate of diffusion of D^+ ions may be calculated from the mobility of the D^+ ion in water, using the following relation due to Nernst (Z.f.physik.Chem., 2 p.631, 1888).

$$D_{\text{D}^+} = .02596 U \times 10^{-5} \text{ cm}^2/\text{sec.},$$

where the mobility, U, is expressed in electrical units. From the values of Lewis and Doody (J. Am. Chem. Soc., 55, p.3504, 1933) the mobility of D^+ ion in 2% heavy water at 14°C is approximately 290.

Hence $D_{D^+} = 7.53 \times 10^{-5} \text{ cm}^2/\text{sec}$,

Now, since the total concentration of hydrogen ion ($D^+ + H^+$) is everywhere 1 normal in the diffusing liquid, the diffusion gradient for the deuterium ions must always be $1/55.5$ of that for the heavy water molecules.

The appropriate diffusion equation is then,

$$\begin{aligned} \frac{ds}{dt} &= D_{D_2O} A \frac{dc}{dx} + D_{D^+} A \left(\frac{1}{55.5} \frac{dc}{dx} \right) \\ &= A \frac{dc}{dx} (D_{D_2O} + \frac{1}{55.5} D_{D^+}) \end{aligned}$$

Also, since the analysis for the concentrations c and c' makes no discrimination as to whether these were originally ions or molecules, the experimental value of D determined from equation (2) will be equal to

$$D_{D_2O} + \frac{1}{55.5} D_{D^+}$$

An increase of $(1/55.5)D_{D^+}$ (i.e. $0.14 \times 10^{-5} \text{ cm}^2/\text{sec.}$) in the value of the diffusion coefficient for pure water would therefore be expected from the experiments in normal H_2SO_4 .

The average value obtained at 13.5°C (viz. 1.70) is however smaller than the value for the diffusion of pure water at the same temperature (viz. 1.77) by $0.07 \times 10^{-5} \text{ cm}^2/\text{sec}$. The total discrepancy $(0.14 + 0.07) \times 10^{-5} \text{ cm}^2/\text{sec}$. is quite outside the possible experimental error. It was evident from this that the presence of the $SO_4^{=}$ ion must exert an electrostrictive effect on the water molecules. In order to determine the magnitude of the effect diffusion experiments were

done in the presence of normal Na_2SO_4 (table 6). A reduction in the value of D for pure water of $0.12 \times 10^{-5} \text{ cm}^2/\text{sec.}$ (at 13.85°C) was obtained. This decrease is not as large as that obtained in the H_2SO_4 experiments, but it is sufficient to bring the discrepancy in the latter experiment within the possible experimental error.

The diffusion coefficient was determined by the latter method at $0.3, 14.3$ and 25°C .

(3) The diffusion coefficient was also determined in the presence of normal H_2SO_4 and normal Na_2SO_4 .

(4) The results indicate that the diffusion of water is a purely molecular process, and that the rate of diffusion of hydrogen ions is not great enough to cause an apparent increase.

(5) The diffusion results are discussed in relation to Einstein's Diffusion equation.

(6) By means of a simple theoretical calculation the activation energy required for the diffusion of water molecules is estimated.

SUMMARY.

- (1) Experiments on the concentration of deuterium by the electrolysis of water are described.
- (2) Two methods of determining the rate of diffusion of deuterium oxide in water were tried. Of these the cylinder method of Graham proved impracticable, while the other, Northrup and Anson's sintered glass plate method, gave satisfactory results. The diffusion coefficient was determined by the latter method at 0.1, 14.3 and 25° C.
- (3) The diffusion coefficient was also determined in the presence of normal H_2SO_4 and normal Na_2SO_4 .
- (4) The results indicate that the diffusion of water is a purely molecular process, and that the rate of diffusion of hydrogen ions is not great enough to cause an apparent increase.
- (5) The diffusion results are discussed in relation to Einstein's Diffusion equation.
- (6) By means of a simple theoretical calculation the activation energy required for the diffusion of water molecules is estimated.

Note onThe Refractive Index of Deuterium Gas.Experimental:

One of the physical properties of heavy hydrogen that has so far not been determined is the refractive index. The apparatus to be described here was designed with two aims in view, the first being to recover, by electrolysis, heavy water from mixtures which contained H_2SO_4 and such organic compounds as methyl and ethyl alcohol, acetone, phenol, ethyl acetate and acetic acid, the second purpose being to determine the refractive index of the heavy hydrogen gas which is liberated during the electrolysis.

The apparatus (see fig. 9) which was made of soft glass except for the combustion tube D and L, was designed to avoid as much as possible rubber connections. From C to F the apparatus was made in duplicate and the two pieces coupled together so that the hydrogen liberated in one cell and the heavy hydrogen in the other underwent identical treatments before entering the opposite sides of the Interferometer gas tubes at G and G'. The U-shaped cells (B) were narrowed at the bend to permit as much electrolyte being electrolysed as possible and were fitted with platinum electrodes of about $\frac{1}{4}$ sq. cm. area, the cathodes being attached to stout platinum wires sealed in ground glass joints. The tubes D, in which traces of oxygen were combined

with hydrogen, were filled with platinised asbestos and electrically heated so that a temperature of 250-300°C was maintained inside. The traps C were cooled in liquid air in order to condense gases such as ethane which might be produced by secondary reactions at the cathode and also to collect any liquid vapour carried by the gas stream. The traps E were cooled in ether-CO₂ mixtures to remove water formed in the tube D. In order that the gases might be at room temperature when entering the gas tubes, spirals immersed in water, were placed at F. The two streams leaving the gas tubes were led to the opposite limbs of a mercury manometer (H) by which any difference in their pressure was immediately detected, the light hydrogen then passing into the atmosphere through the constriction J, which just touched a mercury surface, while the heavy hydrogen passed to the CuO tube L, which was kept at 500°C by an electric furnace. The heavy water so produced was frozen out in the U-tube M, cooled in an ether-CO₂ mixture.

A slow stream of dried nitrogen was introduced occasionally at K in order to carry over the water vapour completely. At the anode side of the heavy water cell a small trap (A), cooled in an ether-CO₂ mixture was fitted to condense vapour carried over in the oxygen stream. Before starting experiments all

the ground glass joints were greased lightly with Apiezon grease, sealed over with picein wax, and the apparatus then tested for leaks.

The gas tubes mentioned above were those belonging to the Rayleigh Interferometer which was set up beside the apparatus so that readings could be taken during the whole course of the experiment.

The cells, filled first of all with ordinary water to which a little KOH had been added, were connected in series and electrolysed at a current of 1 amp. for 6 hours. The heating coils at C were not put on till after 3 or 4 hours so that the apparatus was filled with hydrogen without risk of explosion. During this run the zero-reading on the interferometer with ordinary hydrogen in both sides of the gas tubes was determined, viz. 978.1, while in addition it was ascertained that no leakage took place through the rubber tubing connecting the gas tubes to the apparatus and also, it was found that a correct reading of the interferometer could be made while the gases were streaming through the tubes.

The mixture of heavy water and organic impurities was now placed in the appropriate cell and since the liquid contained H_2SO_4 no other electrolyte was added. As the hydrogen was displaced by the heavy hydrogen the interferometer reading changed steadily until after 20 hours, (at a current of .5 amp), a

reading of 954 was attained and did not vary during the remainder of the electrolysis.

Another supply of heavy water, mixed with acetone, was now added and electrolysis re-commenced. Using a current of .7 amp. the course of the readings was as follows:-

Hours	2	7	11	14½	20
Reading	966	963	960.5	954.1	954.1

The liquid recovered in the U-tube M was collected in two fractions (a) that which came off before the reading became steady at 954.1, and (b) all that was subsequently produced.

The analysis of the small samples of water obtained was made using the Interferometer, which was calibrated for this experiment by determining the readings in a 1 cm. cell, of the following D_2O solutions of known concentration.

Shift due to 99.1 mol% D_2O = 1094 drum divisions

Shift due to 1 mol% D_2O = 14 " "

Hence the shift corresponding to 100% D_2O is 1107.

(The 99.1% D_2O was from a stock obtained from Norway: the concentration of the 1% D_2O was determined by density methods.)

The analysis of the fractions (a) and (b) was as follows:-

Shift due to fraction (a) (volume = 6cc) =
862.5 drum divisions

Hence this sample is approximately 78% D_2O .

Shift due to fraction (b) (volume = 2cc) = 1110
drum divisions.

Hence this sample must be 100% D₂O.

The difference of 3 drum divisions between the reading for 100% D₂O and for fraction (b) is attributable to experimental error since in this region the fringes are very indistinct.

The difference between the refractive indices of ordinary and 100% hydrogen ($\Delta\mu$) corresponding to the interferometer shift (978.1 - 954.1 = 24.0) drum divisions is given by the formula:-

$$\Delta\mu = \frac{N\lambda}{L} \times 10^{-8},$$

where N is the number of fringes corresponding to a shift of 24.0 when a monochromatic light source of wavelength λ Ångströms is used, and L is the length of the gas tubes, viz. 75 cms. The correction, which in general would be applied to this formula to take account of dispersion, is completely negligible in this experiment where a shift of less than two fringes is involved.

The calibration of the drum reading was made using the wavelength 5461 Å, suitably filtered from a mercury arc source. The following readings were obtained for consecutive fringes:-

934	948.2	962.1	976.5	991.1
Difference	14.2	13.9	14.4	14.6

∴ Average difference = 14.25

$$\text{Hence } N = \frac{24.0}{14.25}$$

$$\begin{aligned} \Delta\mu &= \frac{24.0}{14.25} \cdot \frac{5461}{75} \times 10^{-8} \\ &= (123 \pm 2) \times 10^{-8} \end{aligned}$$

Now, from the design of the instrument, a shift in the direction found indicated that the heavy hydrogen had a smaller refractive index than ordinary hydrogen. The refractive index for H_2 at $\lambda = 5461$ given by the I.C.T. is

$$1.00013966 \text{ (273}^\circ\text{A, 760 mm. press.)}$$

Hence the refractive index of deuterium at $\lambda = 5461$ is 1.0001384(3).

SUMMARY.

1. An apparatus suitable for separating heavy water from mixtures with organic compounds is described.
2. The refractive index of heavy hydrogen at the wavelength 5461 \AA is found to be appreciably smaller than that of ordinary hydrogen and to have the value 1.0001384.

In conclusion I wish to express my gratitude to Dr. J.A.V. Butler for his valuable guidance and encouragement during the course of this research. I have also to express my thanks for grants received from the Research Fund of the Chemical Society and the Earl of Moray Endowment. Finally, I would acknowledge my indebtedness to the Carnegie Trust for the grant of a Research Scholarship, during the tenure of which, this work has been performed.