

CCXCVI.—*Remarks on the Electrical and Mechanical Conditions in the Neighbourhood of a Dissolved Ion.*

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THE calculations to be summarised below arose in connexion with certain work on the electrolytic equilibria of acids (this vol., p. 2153), and again in the course of some studies on the dynamics of the saponification of esters (this vol., p. 2170); and other applications can be foreseen. Reference may be made to these papers for the general introductory remarks which might have been included here.

The problem is to calculate the effect of the radially oriented and attracted solvent molecules surrounding an ion on the local electrical conditions. We shall find that the calculation necessarily includes a consideration of the local mechanical conditions.

For the purposes of the electrical calculation we may define an "ideal state" as follows: (1) the solvent is unassociated; (2) its molecules are optically and electrically isotropic; (3) the local inner field (Raman) is isotropic; (4) the solvent is incompressible. We may assume that if conditions (1), (2), and (3) be fulfilled Mosotti's law will be obeyed; the non-fulfilment of (1) is the main cause, whilst departures from (2) and from (3) are subsidiary causes, of deviations from Mosotti's principle. An "ideal" solvent may, therefore, also be defined as one which obeys Mosotti's law and is incompressible.

We shall have to envisage deviations from all these conditions, but it is convenient to assume their fulfilment in the first instance in order to obtain a point of departure.

We require to evaluate the potential Φ in the environment of an ion because then we can derive the mutual potential energy of two neighbouring ions, and this is what is required in problems on ionic reactions. The principles of the calculation under "ideal" conditions are well known (Debye, "Polar Molecules," 1929). On account of Gauss's theorem we have

$$D = q/r^2 (1)$$

where D is the induction at any field-point, q the charge on the ion, and r the distance of the point from the charge. The electric

intensity, E , and the inner field, F , are given by the field-equations

$$D = E + 4\pi I \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$F = E + \frac{4}{3}\pi I \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where I is the intensity of polarisation. The vectors of D , E , F , I , and r correspond in direction at all points. The further equation necessary for the calculation of the four electrical vectors in terms of r is found in Debye's relation between I and F :

$$I = \nu \left\{ \gamma F + \mu \left(\coth \frac{\mu F}{kT} - \frac{kT}{\mu F} \right) \right\} \quad . \quad . \quad . \quad (4)$$

Here, μ is the electric moment of a molecule, γ its coefficient of polarisability (induced moment per unit field), ν the number of molecules per c.c., k is Boltzmann's constant, and T is the absolute temperature. These quantities being supposed known, equations (1)—(4) give E for every point in the field; and then the definition of E as $-\text{grad}\Phi$ gives Φ in the form

$$\Phi = -\int_r^\infty E \cdot dr \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It is well known that, if powers of F higher than the first are deleted from the development of (4), and (2), (3), and the residue of (4) are solved together, the equation for ratio D/E , which is the dielectric constant ϵ , may be expressed (Debye) thus:

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho} = \frac{4\pi N}{3} \left\{ \gamma - \frac{\mu^2}{3kT} \right\} \quad . \quad . \quad . \quad (6)$$

where M is the molecular weight and ρ the density of the solvent, whilst N is Avogadro's number. The dielectric constant which would obtain in the absence of molecular orientation, may, following Maxwell, be expressed as the square of a refractive index, n_∞ , and may be connected with γ by omitting the μ -term from (6):

$$\frac{n_\infty^2 - 1}{n_\infty^2 + 2} \cdot \frac{M}{\rho} = \frac{4\pi N \gamma}{3} \quad . \quad . \quad . \quad . \quad (7)$$

Thus γ may be evaluated provided n_∞ can be identified. There appears to be some dubiety about the value of n_∞ . In the case of water, some investigators, *e.g.*, Ebert (*Z. physikal. Chem.*, 1924, **113**, 1), have adopted Rubens's value, $n_\infty = 2.0$, obtained from measurements of refractive index in the far infra-red; others, *e.g.*, Malsch (*Ann. Physik*, 1927, **84**, 841), have used $n_\infty = 1.3$, the value obtained when the refractive index in the visible region is extrapolated to infinite wave-length either graphically or by a dispersion formula applicable to the visible region. As Debye has pointed out (*loc. cit.*), neither method is correct, and the truth must lie between the two

results : for n_{∞} is supposed to be the refractive index for long waves due to *all* forms of molecular polarisation, but *without orientation* ; it should therefore include an allowance for the dispersion arising from atom-polarisation, but it should exclude the dispersion caused by molecular rotation. The absorption bands due both to atom-polarisation and to rotation are in the infra-red, and their effects on the refractive index are difficult to distinguish : the higher estimate of n_{∞} includes both influences and the lower value excludes both. For these reasons we reverted to equation (6) and, applying Jona's data (*Physikal. Z.*, 1919, **20**, 14) for the dielectric constant of water vapour at different temperatures, evaluated γ directly. The corresponding value of n_{∞} is 1.51 in accordance with equation (7). This method of computation assumes that Lorentz's law applies to water, which it does approximately ; corrections for the deviations from this law are considered later.

The value of μ cannot be similarly obtained from data relating to water vapour because the departures from Mosotti's law are too great : association, though it has very little influence on the mean contribution of a molecule to the refractive index, has a large effect on the dielectric constant because it interferes with independent molecular orientation. We have to calculate an effective moment μ , which is obtained by fitting equation (6) to data relating to the liquid at the required temperature, and even then, as will appear later, μ has ultimately to be treated, not as a constant, but as a function of density. It will be seen that in adopting this plan (even apart from allowances for the density-variation of γ and μ) we are already taking account in an approximate way of the main cause of deviation from Mosotti's law.

The water molecule is anisotropic. In the case of liquids whose molecules are not isotropic, Debye's equation connecting I with F takes a more complex form than is presented by (4). We shall assume that the dipole axis and two other directions, all mutually perpendicular, may be treated as principal axes of polarisability, for which the coefficients of polarisability are a , b , and c respectively. This supposition may not be strictly accurate owing to molecular distortion by an anisotropic environment, but it is shown later that this point is immaterial. Under the conditions postulated, the equation for I becomes

$$I = v \cdot \frac{\iint e^{\frac{\mu F}{kT} \cos \theta + \frac{F^2}{2kT} f(abc\theta\phi)} \{ \mu \cos \theta + F f(abc\theta\phi) \} \cdot \sin \theta \cdot d\theta \cdot d\phi}{\iint e^{\frac{\mu F}{kT} \cos \theta + \frac{F^2}{2kT} f(abc\theta\phi)} \cdot \sin \theta \cdot d\theta \cdot d\phi} \quad (8)$$

where θ is the angle between the dipole axis of a molecule and the

field-direction, ϕ is a longitude in the molecule referred to the same axis as polar axis, and

$$f(abc\theta\phi) = a \cos^2 \theta + b \sin^2 \theta \cdot \cos^2 \phi + c \sin^2 \theta \cdot \sin^2 \phi$$

One of the three equations necessary for the numerical evaluation of the molecular constants a, b , and c is readily obtained: on deleting powers of F higher than the first from the development of (8) and comparing the result with (6), it is found (Debye, *loc. cit.*) that

$$a + b + c = 3\gamma \dots \dots \dots (9)$$

A relation due to Gans (*Ann. Physik*, 1921, **65**, 97) enables two other equations to be derived from optical properties. Owing to the inertia of the electrons the coefficients, a', b' , and c' of optical polarisability are not the same as a, b , and c ; in other words, the optical constants are subject to dispersion and have to be extrapolated to large wave-length in order to yield the statical-electrical constants a, b , and c . Gans's relation is

$$\frac{a'}{a} = \frac{b'}{b} = \frac{c'}{c} = \frac{(n^2 - 1)/(n^2 + 2)}{(n_\infty^2 - 1)/(n_\infty^2 + 2)} \dots \dots \dots (10)$$

where n is the refractive index for the wave-length, λ , to which a', b' , and c' apply.

From the theory of light-scattering by liquids, the depolarisation-factor, v , for transversely scattered light is given by the equation

$$v = \frac{6M[(a' - b')^2 + (b' - c')^2 + (c' - a')^2]}{10kT\beta N\rho(a' + b' + c')^2 + 7M[(a' - b')^2 + (b' - c')^2 + (c' - a')^2]} \dots (11)$$

where β is the compressibility of the liquid at the temperature and pressure at which v is measured. The combination of equations (7), (9), and (10) gives

$$a' + b' + c' = \frac{9M}{4\pi N\rho} \cdot \frac{n^2 - 1}{n^2 + 2} \dots \dots \dots (12)$$

and on substituting from (12) in (11) and again taking (10) into account, we have

$$(a - b)^2 + (b - c)^2 + (c - a)^2 = \frac{405kT\beta M}{8\pi^2 N\rho} \cdot \left(\frac{n_\infty^2 - 1}{n_\infty^2 + 2}\right)^2 \cdot \frac{v}{6 - 7v} \dots (13)$$

According to the theory of electrical double refraction, the Kerr constant, B , is given by the equation

$$B = \frac{\pi N\rho(n^2 + 2)^2 (\epsilon + 2)^2}{27Mn\lambda} (\Theta_1 + \Theta_2) \dots \dots (14)$$

where

$$\Theta_1 = \frac{1}{45kT} [(a - b)(a' - b') + (b - c)(b' - c') + (c - a)(c' - a')] \dots (15)$$

and

$$\Theta_2 = \frac{1}{45k^2T^2} [(a' - b')(\mu_a^2 - \mu_b^2) + (b' - c')(\mu_b^2 - \mu_c^2) + (c' - a')(\mu_c^2 - \mu_a^2)] \dots (16)$$

The Kerr constant is, of course, subject to dispersion, and both B and the refractive index, n , must correspond with λ . The application of equations (10) and (13) to equation (15) shows that Θ_1 has the value

$$\Theta_1 = \frac{9\beta M}{8\pi^2 N \rho} \cdot \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \cdot \frac{n^2 - 1}{n^2 + 2} \cdot \frac{v}{6 - 7v} \quad (17)$$

If one of the axes of polarisability is taken as coincident with the dipole axis (see above), $\mu_a = \mu$ and $\mu_b = \mu_c = 0$, and, in view of (10), the expression for Θ_2 becomes

$$\Theta_2 = \frac{\mu^2}{45k^2 T^2} \cdot \frac{n^2 - 1}{n^2 + 2} \cdot \frac{n_\infty^2 + 2}{n_\infty^2 - 1} (2a - b - c) \quad (18)$$

The remaining equation required for the evaluation of the constants a , b , and c is now obtained by combining (14), (17), and (18) :

$$2a - b - c = \frac{1215k^2 T^2 M n B \lambda}{\pi \mu^2 N \rho (\epsilon + 2)^2} \cdot \frac{n_\infty^2 - 1}{(n^2 - 1)(n^2 + 2)(n_\infty^2 + 2)} - \frac{405k^2 T^2 M \beta}{8\pi^2 \mu^2 N \rho} \cdot \frac{(n_\infty^2 - 1)^2}{(n^2 + 2)} \cdot \frac{v}{6 - 7v} \quad (19)$$

Table I contains a number of the numerical values employed in these calculations; the upper portion includes those required for the evaluation of the constants of the ellipsoids of statical and optical anisotropy, and the derived constants are at the foot of the table. Kerr constants and depolarisation factors have been used separately for the calculation of the constants of anisotropy of optically spheroidal molecules (*e.g.*, diatomic and linear triatomic molecules), but the case of water is more complex and does not appear previously to have been computed.

TABLE I.

$B = 2.67 \times 10^{-7}$	$n = 1.330$	$v = 0.085$	$\mu = 0.7611 \times 10^{-18}$
$M = 18.02$	$n_\infty = 1.510$	$\beta = 45.4 \times 10^{-12}$	$\rho = 0.9971$
$N = 6.062 \times 10^{23}$	$n^2 = 1.769$	$r = 2.129 \times 10^{-24}$	$\frac{\partial n_\infty}{\partial p} = 15.36 \times 10^{-12}$
$T = 298.2$	$n_\infty^2 = 2.280$	$\epsilon = 78.1$	
$k = 1.371 \times 10^{-16}$	$q = 4.774 \times 10^{-10}$	$\lambda = 7.00 \times 10^{-5}$	$\frac{\partial \epsilon}{\partial p} = 46.7 \times 10^{-10}$
Ellipsoid (λ)	$a' = 1.449 \times 10^{-24}$	$b' = 1.630 \times 10^{-24}$	$c' = 1.277 \times 10^{-24}$
Ellipsoid (∞)	$a = 2.174 \times 10^{-24}$	$b = 2.389 \times 10^{-24}$	$c = 1.873 \times 10^{-24}$

The influence of anisotropy on the electric field is small (indeed over much of the region of the field with which we are concerned it is insignificant), and for this reason the question as to whether an anisotropic molecular environment would create a finite angle between the dipole axis and the corresponding principal axis of polarisability is unimportant, as this effect could only make a minute change in an already small correction. Furthermore, the circum-

stance that molecular anisotropy can be treated as a correction greatly simplifies computation from the formulæ. For large radial distances equation (4) may be replaced by its second approximation (20), the influence of anisotropy being neglected altogether:

$$I = \nu \left[\left\{ \gamma + \frac{\mu^2}{3kT} \right\} F - \frac{\mu^4}{45k^3T^3} \cdot F^3 \right]. \quad (20)$$

For most smaller distances it is sufficient if we employ (4) without approximating, and then estimate the correction for anisotropy by comparing the results given by the second approximation of (4), namely (20), with those derived from the second approximation of (8), namely (21):

$$I = \nu \left[\left\{ \gamma + \frac{\mu^2}{3kT} \right\} F + \left\{ \frac{(a-b)^2 + (b-c)^2 + (c-a)^2}{45kT} + \frac{2(2a-b-c)\mu^2}{45k^2T^2} - \frac{\mu^4}{45k^3T^3} \right\} F^3 \right] \quad (21)$$

The above, of course, is without prejudice to the modifications which all these equations have still to undergo in order to take account of influences yet to be considered.

One of the most important of these arises from the excess of internal pressure due to the attraction of the ion for the oriented water dipoles. The mechanical force on a dipolar molecule in an electric field is given by $(\mathbf{m} \text{ grad}) \mathbf{E}$, where \mathbf{m} is the total moment (permanent plus induced) of the molecule (vectors are represented in heavy type). Since our electrical field is radial, the only finite component of the tensor derived from \mathbf{E} is $\partial E_r / \partial r$, and hence by the definition of the vector gradient of a vector, the direction of the force is that of $-\mathbf{r}$ and its magnitude is $-m_r \partial E_r / \partial r$. Since the average value of m_r is I/ν , which, by equation (2), is $(D - E)/4\pi\nu$, the average force on a molecule is $-\{(D - E)/4\pi\nu\} (dE/dr)$, and the force on 1 c.c. is ν times this. Hence the excess of internal pressure due to the ion is

$$p = - \left. \begin{aligned} & \frac{1}{4\pi r^2} \int_r^\infty (D - E) \cdot \frac{dE}{dr} \cdot r^2 \cdot dr \\ & = \frac{q}{2\pi r^2} \int_r^\infty \frac{D - E}{dD/dE} \cdot \frac{dr}{r} \end{aligned} \right\} \quad (22)$$

the second form of this equation being derived from the first by the use of equation (1).

The pressure near an ion due to its attraction for the solvent may amount to some thousands of atmospheres, and, owing to the compressibility of the solvent, there will be corresponding changes of density. The compressibility of water is known up to about 10,000 atmospheres. If σ is the density expressed as a multiple of that at

low pressure, it follows from the definition of compressibility, $\beta = -(1/V)(dV/dp)$, where V is the volume occupied by a fixed mass, that

$$\sigma = e^{\int_0^p \beta \cdot dp} \dots \dots \dots (23)$$

Equations (22) and (23) give σ as a function of r , and hence the effect of the additional internal pressure is allowed for (except in so far as this disturbance interacts with that due to deviations from Mosotti's principle—a point considered below) if in equations (4), (18), (20), and (21) we ascribe to v the space-variable value

$$v = \sigma N \rho / M \dots \dots \dots (24)$$

The numerical values of σ and β are shown in Table II.

TABLE II.

$10^{-7} p.$ $10^{12} \beta.$ $\sigma.$			$10^{-7} p.$ $10^{12} \beta.$ $\sigma.$			$10^{-7} p.$ $10^{12} \beta.$ $\sigma.$		
1	45.3	1.00045	150	32.2	1.058	600	17.1	1.177
2	45.2	1.00090	200	29.5	1.075	650	16.1	1.186
5	45.0	1.00225	250	26.9	1.091	700	15.2	1.195
10	44.1	1.0045	300	24.9	1.106	750	14.2	1.203
20	42.9	1.0089	350	23.1	1.120	800	13.3	1.211
30	41.7	1.0133	400	21.7	1.133	850	12.4	1.219
40	40.6	1.0175	450	20.3	1.145	900	11.5	1.226
50	39.5	1.0215	500	19.1	1.156	950	10.6	1.233
100	35.5	1.0410	550	18.0	1.166	1000	9.7	1.240

Owing to departures from Mosotti's hypothesis, γ and μ , which at first were treated as constants, must also be regarded as functions dependent on density and therefore on position. The nature of these functions may be deduced to a first approximation from the pressure coefficients of the refractive index and the dielectric constant.

In the absence of molecular orientation, the deviations from Mosotti's assumption are small, and we may therefore assume that $\partial n_{\infty} / \partial p$ is given sufficiently accurately by the known value of $\partial n / \partial p$ for sodium light (15.36×10^{-12}). Using this figure in conjunction with values β , n_{∞} , etc., already tabulated, it can readily be shown that the variability which must be attributed to γ in order to preserve the form of our equations whilst allowing for the deviations under consideration is expressed by the relation

$$\frac{4}{3} \pi v \gamma = \frac{58.88 + 128.0(\sigma - 1)}{196.9 + 266.0(\sigma - 1)} \dots \dots (25)$$

where v is given by (24) and σ by (23).

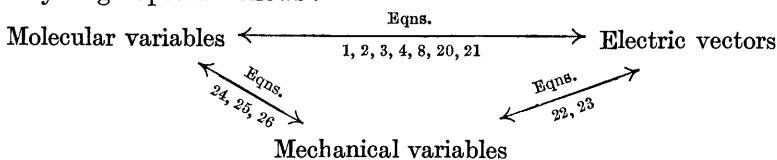
The value of $\partial E / \partial p$ being known also, it can be shown in a similar way that the density-dependence which must be ascribed to μ in order to account for the residual departures from Mosotti's hypothesis

in terms of the equations already given is represented by the expression

$$\frac{4\pi\nu}{9kT}\mu^2 = \frac{77.1 + 177(\sigma - 1)}{80.1 + 180(\sigma - 1)} - \frac{4}{3}\pi\nu\gamma \quad . \quad (26)$$

where ν and γ have the values corresponding with equations (24) and (25) respectively, and σ is given by (23).

For the purposes of numerical computation, the above equations may be grouped as follows:



As it is impossible to eliminate any one set of variables by mathematical methods (*e.g.*, mechanical variables between equations 24—26 on the one hand, and equations 22, 23 on the other), the only way is to proceed by the method of successive approximations, the cycle being traversed repeatedly until a set of variables is deduced which remains the same when the cyclic calculation is performed once more; and this must be done for a sufficient number of field-points to render interpolation possible.

The main result of this calculation is to give E as a function of r , and it is then necessary to evaluate the integral in equation (5) in order to obtain Φ . Runge's process was customarily employed for the calculation of definite integrals, but in the present instance the slow convergence of the function towards the limit ∞ necessitates an alternative method for the evaluation of the upper portion of the integral. This, however, presents no difficulty because it is precisely in this region that the second-approximation equation (20) applies with accuracy.

This equation, on combination with equations (2) and (3), gives the relation

$$\frac{D - E}{D + 2E} = \frac{4}{3}\pi\nu \left[\gamma + \frac{\mu^2}{3kT} - \frac{1}{45} \frac{\mu^4}{k^3 T^3} \cdot F^2 \right] \quad . \quad (27)$$

The term in F^2 in equation (27) is a small correction and hence may be replaced by its first approximation, which is derived by deleting from equation (20) the term in F^3 and combining the residue of the equation with equations (2) and (3). The result is

$$F = D \left[1 + \frac{8}{3}\pi\nu \left\{ \gamma + \frac{\mu^2}{3kT} \right\} \right] \quad . \quad . \quad (28)$$

On eliminating F between equations (27) and (28), solving for E as a function of D , developing the function in ascending odd powers of D

as far as D^3 , and replacing D by its equivalent, q/r^2 , in accordance with equation (1), we obtain the relation

$$E = \frac{1 - \frac{4}{3}\pi v \left\{ \gamma + \frac{\mu^2}{3kT} \right\}}{1 + \frac{8}{3}\pi v \left\{ \gamma + \frac{\mu^2}{3kT} \right\}} \cdot \frac{q}{r^2} + \frac{4\pi v \cdot \frac{\mu^4}{45k^3T^3}}{\left[1 + \frac{8}{3}\pi v \left\{ \gamma + \frac{\mu^2}{3kT} \right\} \right]^2} \cdot \frac{q^3}{r^6} \quad (29)$$

This equation gives E directly, because, in the part of the field for which the relation holds accurately, σ may be taken as unity. In accordance with equation (5), the equation giving Φ in the same region of the field is

$$\Phi = \frac{1 - \frac{4}{3}\pi v \left\{ \gamma + \frac{\mu^2}{3kT} \right\}}{1 + \frac{8}{3}\pi v \left\{ \gamma + \frac{\mu^2}{3kT} \right\}} \cdot \frac{q}{r} + \frac{\frac{4}{5}\pi v \cdot \frac{\mu^4}{45k^3T^3}}{\left[1 + \frac{8}{3}\pi v \left\{ \gamma + \frac{\mu^2}{3kT} \right\} \right]^2} \cdot \frac{q^3}{r^5} \quad (30)$$

When $r \gg 12 \times 10^{-8}$, equations (29) and (30) give results correct to three significant figures, and may be used to replace the system of equations represented in the cyclic scheme on p. 2186.

By employing the numerical data contained in Tables I and II, the following values have been computed :

(i) For $r \gg 12 \times 10^{-8}$, the values of E and Φ are given by

$$\left. \begin{aligned} E &= \frac{6.112 \times 10^{-12}}{r^2} + \frac{6.839 \times 10^{-41}}{r^6} \\ \Phi &= \frac{6.112 \times 10^{-12}}{r} + \frac{1.368 \times 10^{-41}}{r^5} \end{aligned} \right\} \cdot \cdot \quad (31)$$

(ii) For $r \ll 12 \times 10^{-8}$, the values of p , σ , E , and Φ are as shown in Table III. (It may be noted that, c.g.s. units having been employed throughout, the pressure are in dynes/cm.² and require division by 1.014×10^6 for conversion to atmospheres.)

In the applications for which the functions tabulated were computed, it is necessary to calculate the potential energy, W' , of a second ion, of charge q' , in the field of the first. We know that this is the sum of an infinite series of terms diminishing in importance, of which the first, and most important, is $q'\Phi$; we also know that the value of each term in the series diminishes with increasing distance more rapidly than the one before it. We intend to neglect all terms after the first, and it is therefore necessary to investigate the order of magnitude of the second term for the distances with which we are concerned. The reason why we are forced to neglect the higher terms is because there is no known means of evaluating the molecular electric constants they contain. Thus the second term is $-(\mathbf{m}'\mathbf{E})$, where \mathbf{m}' is the effective electric moment (permanent plus induced)

TABLE III. (32)

$r \times 10^8$ (cm.).	p (c.g.s.).	σ ($\sigma = 1, p = 0$).	E (e.s.u.).	Φ (e.s.u.).
2.25	11.4×10^9	1.27	1.83×10^5	1.55×10^{-3}
2.50	7.0	1.20	1.33	1.16
2.75	4.2	1.15	9.59×10^4	8.78×10^{-4}
3.00	26.3×10^8	1.10	6.96	6.73
3.25	16.6	1.067	5.04	5.24
3.50	10.7	1.043	3.64	4.17
3.75	6.8	1.028	2.65	3.39
4.00	4.5	1.019	1.96	2.83
4.25	29.9×10^7	1.013	1.46	2.40
4.50	20.4	1.0089	1.11	2.08
4.75	14.3	1.0063	8.53×10^3	1.83
5.00	10.1	1.0045	6.75	1.65
5.50	5.6	1.0025	4.43	1.38
6.00	3.2	1.0015	3.15	1.19
6.50	20.7×10^6	1.00097	2.35	1.06
7.00	14.1	1.00064	1.82	9.52×10^{-5}
7.50	9.7	1.00045	1.46	8.71
8.00	7.0	1.00032	1.21	8.04
8.50	5.2	1.00023	1.02	7.49
9.00	3.9	1.00017	8.80×10^2	7.01
9.50	3.0	1.00013	7.67	6.61
10.00	2.4	1.00010	6.76	6.24
11.00	1.6	1.00007	5.40	5.64
12.00	1.1	1.00005	4.44	5.15

of the ion and the parentheses denote a scalar product; but we know nothing about the permanent part of this moment, which is sure to be the greater portion of it in the case of such ions as OH_3^+ and OH^- which are the centre of our interest at present. However, on the assumption that the dipole moments of the hydrogen and hydroxide ions are not very different from that of water (just as the moments of chloroform and methyl chloride are not very different from that of methylene chloride) it is possible to calculate the order of magnitude of $-(\mathbf{m}'\mathbf{E})$, and of its effective mean value having regard to the statistical distribution of the orientations of the dipole axes, and thus to show that the effect of this energy term is negligible except at very short distance; at which, in the applications for which these calculations are intended, our computed results cannot in any case be expected to correspond to reality because of the neglect of internal polar transmission in the ion responsible for the electric field.

Besides these electrostatic contributions, $q'\Phi - (\overline{\mathbf{m}'\mathbf{E}}) + \dots$ etc., to the energy (the bar denotes an average), there is also a mechanical contribution due to the non-uniformity of the pressure-field. This is also expressible as the sum of an infinite series of terms of progressively diminishing importance and increasing rate of diminution with increasing distance. It is necessary to investigate the order of magnitude of the first term of this series. The value of the first term is $+(\overline{\mathbf{m}_w\mathbf{E}})V'/V_w$, where \mathbf{m}_w is the effective electric

moment (permanent plus induced) of a water molecule, and the coefficient of the scalar product is the ratio of the molecular volumes of the ion and of water. This term is obviously of the same order of magnitude as the second term of the series of electrostatic contributions, and for the same reasons may be neglected for the present purposes. *A fortiori*, the combination of terms, $-\overline{(\mathbf{m}'\mathbf{E})} + \overline{(\mathbf{m}_w\mathbf{E})}V/V_w$, may be disregarded, because the constituents are always, arithmetically as well as algebraically, of opposite sign.

There is experimental confirmation of this conclusion in the applications, described in the accompanying communications, to the electrolytic equilibria of acids and to the dynamics of the saponification of esters. The formula

$$W = q'\Phi - \overline{(\mathbf{m}'\mathbf{E})} + \dots + \overline{(\mathbf{m}_w\mathbf{E})}V/V_w - \dots \quad (33)$$

has connexion with both problems; but there is this difference in its numerical equivalent in the two cases, namely, that the relations of the signs (like or unlike) of the values of the second and third of the fully expressed terms on the right-hand side of (33) to the sign of the value of the first term are opposite. Therefore the neglect of the second and third terms would be expected to introduce a positive error in one problem and a negative error in the other, and, if these terms were not small relatively to the first term, corresponding values of r calculated by the two methods should be different. On the contrary, it is shown that in every case in which the comparison is pertinent (*i.e.*, excluding very short distances) the results are the same.

Finally, it should be pointed out that Φ , and the vectors and tensors derived from it, are also expressible as infinite series of which we have only considered the first term. No further consideration need be given to \mathbf{E} since this occurs only in the negligible terms of (33); Φ , however, has the form

$$\Phi = \psi(q,r) + \psi_1(m,r) + \dots \quad (34)$$

and the values we have formulated and tabulated in (31) and (32) as values of Φ are really values of $\psi(q,r)$. The order of magnitude of the second term on the right-hand side of (34) therefore requires examination. It is not difficult to show that if m , the moment of the ion responsible for the field, is of the same order of magnitude as m' (and this would almost certainly be true in the cases with which we are immediately concerned), then $q'\psi_1(m,r)$ is of the same order of magnitude as $\overline{(\mathbf{m}'\mathbf{E})}$; that is, it is negligible except at very short distances at which, in our applications, internal polar disturbances inevitably enter. Indeed, it is obvious that the calculation of the second and following terms on the right-hand side of

(34), and of the second and later terms on the right-hand side of (33), and the evaluation of the interaction of these two sets of terms with each other and the primary terms, are all parts of the problem taking theoretical account of internal polar transmission.

The result of this investigation into the order of magnitude of the higher terms in (33) and (34) is, then, that beyond the range of effects due to internal polar propagation, the mutual potential energy of two ions may be computed from the expression

$$W = q'\psi(q,r) \dots \dots \dots (35)$$

where ψ has the values attributed to Φ in (31) and (32).

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[Received, June 29th, 1931.]
