

# On the Activity Coefficient for Ions

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1. In the year 1887 Arrhenius presented his famous hypothesis according to which the ions in a solution of electrolytes are present in the free state. During the next three decades this hypothesis has become an indispensable part of physics and chemistry, and even to-day it is a fruitful working hypothesis, which shows the power of the original conception. In the course of time, however, the hypothesis has encountered some difficulties, especially in the explanation of the properties of strong electrolytes. In view of recent work (*cf. ref.*<sup>1</sup>), these difficulties have been resolved on consideration of the effects that must be produced on the properties of the solutions of electrolytes by the electric forces between ions. These effects may be taken into account by means of coefficients expressing the relation between the real value of the property in question and the value the property should have had supposing the electric forces did not act between the ions. Thus the *activity coefficient*  $f_a$  is a measure of the effect of the interionic forces on the activity of the ions; the *conductivity coefficient*  $f_\kappa$  is a measure of the influence of the interionic forces on the conductivity; the *osmotic coefficient*  $f_o$  is a measure of the influence of the interionic forces on the osmotic pressure, etc.

2. It is of great importance to calculate the values of these coefficients from the point of view of our kinetic conceptions of the solutions and to deduce relations between them. And it is of no less importance to determine the values of these coefficients experimentally.

Milner<sup>2</sup> has formed a theory for the osmotic coefficient. This theory does not lead to a simple expression for the coefficient, but it has enabled Milner by numerical calculation to determine approximately the value of the coefficient in case of an electrolyte composed of monovalent ions up to the concentration 0.2 molar. Milner's calculated values are with a fair approximation rendered by the formula

$$1 - f_o = 0.27 \sqrt{c}, \quad (1)$$

in which  $c$  is the molar concentration. This may be seen from table 1.

If we suppose that the strong electrolytes are completely dissociated into ions we may determine the value of the osmotic coefficient by means of freezing-point determinations. From Noyes's and Falk's excellent exposition<sup>3</sup> it thus appears that the osmotic coefficient of all electrolytes with monovalent ions may, with a fair approximation, be given by the formula

$$1 - f_o = k \sqrt[3]{c}, \quad (2)$$

Table 1. Value of  $1 - f_o$

$c$	$1 - f_o$ Milner	$0.27 \sqrt[3]{c}$	$0.17 \sqrt[3]{c}$
0.0001	0.0028	0.0027	
0.001	0.0087	0.0085	
0.01	0.0265	0.027	0.037
0.1	0.081	0.085	0.079
0.2	0.112	0.121	0.099

in which  $k$  varies between 0.146 and 0.225 the mean being 0.17. Although this formula and Milner's are different in form they both give approximately the same values for  $f_o$  within the limits of concentration where both experiments and Milner's calculation are fairly reliable, viz. 0.01  $M$  — 0.1  $M$  (see table 1). This fact must be looked upon as a support for the assumption that the strong electrolytes are *completely dissociated* or, at any rate, are much more dissociated than originally assumed.

When the expression for the osmotic coefficient is known, the formula for the activity coefficient may be deduced by means of the following thermodynamic relation:

$$f_o + c \frac{df_o}{dc} = 1 + c \frac{d \ln f_a}{dc}. \quad (3)$$

If this be combined with equation 2 the following expression is obtained:

$$\ln f_a = -4k \sqrt[3]{c}. \quad (4)$$

In the case of potassium chloride we have

$$1 - f_o = 0.146 \sqrt[3]{c}. \quad (5)$$

From this we obtain:

$$\log f_a = -0.25 \sqrt[3]{c}.$$

This formula can be controlled by measurements of concentration cells. In the case of potassium chloride I obtained, in this way, a confirmation of the formula as far as 0.01 and 0.1 molar solutions are concerned.

3. It would be of great value to obtain a relation between the conductivity coefficient and the other two coefficients. Last year this was tried from two different quarters. But to my judgement the results obtained are not correct.

Milner<sup>4</sup> has tried to show that the conductivity coefficient must equal  $P/P_0$ , where  $P$  is a quantity which he calls the pressure of the free ions, and  $P_0$  the osmotic pressure in the absence of ionic forces. Milner was unable to see clearly the experimental significance of his  $P$ ; but in my opinion there is no doubt but that  $P/P_0$  must equal the activity coefficient. If Milner's result were right then the conductivity coefficient had to be equal to the activity coefficient, and the hitherto general use of the conductivity coefficient, "conductivity degree of dissociation", in calculating chemical equilibria, etc., would be justified not only in the case of weak electrolytes, which actually are incompletely dissociated, but also in the case of strong, completely dissociated electrolytes. However, this result seems rather doubtful. Although it appears from the available experimental data that a certain proportionality exists between  $f_\mu$  and  $f_a$ ,  $f_\mu$  is as a rule somewhat nearer to 1 than  $f_a$ . A critical examination of Milner's considerations, at which Professor N. Bohr lent me valuable assistance, convinced me that the line of argument is not right. In the first place Milner's expressions for the number of "views" which enter and leave the configuration  $P$  in the time  $\tau$  are wrong. Secondly, Milner is not right in identifying  $u_0$  with the experimentally determined conductivity at zero concentration. It is hardly possible, I think, to obtain a result by pursuing Milner's path.

Another attempt was made by Inanendra Chandra Ghosh.<sup>5</sup> He tries to show that

$$i = n(1 + \frac{1}{3} \ln f_\mu), \quad (6)$$

in which  $i$  is van Hoff's old coefficient and  $n$  the number of ions in the electrolyte. Since  $f_0$  equals  $\frac{i}{n}$ , Ghosh's equation may be written

$$f_0 = 1 + \frac{1}{3} \ln f_\mu. \quad (7)$$

Ghosh assumes that the electricity is conducted only by those ions the kinetic energy of which is greater than the average potential of the interionic forces per ion. Here "potential" is the work which must be *done* to separate the ions. This bold and, in my opinion, unwarranted assumption gives Ghosh

$$f_\mu = e^{-\frac{A}{nRT}}, \quad (8)$$

where  $A$  is the potential of the ionic forces per gram-molecule. Since  $A$  further

is equal to the virial of the interionic forces we have according to Clausius, for the osmotic pressure of the ions,  $P$ :

$$PV = nRT - \frac{1}{3}A, \quad (9)$$

which by combination with equation 8 gives:

$$i = \frac{PV}{RT} = n(1 + \frac{1}{3} \ln f_{\mu}). \quad (10)$$

On combining formulae 7, 2, and 4, the following formula may be deduced:

$$\ln f_a = \frac{4}{3} \ln f_{\mu} \quad (11)$$

This result agrees better with the experiments than  $f_a = f_{\mu}$ ; this better agreement, however, can hardly make Ghosh's bold assumptions probable.

Ghosh shows that formula 8 gives the proper value of  $f_{\mu}$  when calculating  $A$  in the following way: We imagine the ions in a binary electrolyte arranged like the atoms in a potassium chloride crystal, and the ions in a ternary electrolyte like the ions in fluorspar, and we further assume that the ions of each salt-molecule form a completely saturated ionic pair. I am not, on this occasion, going to enter more fully into these singular assumptions; I only want to state that the formulae for  $f_{\mu}$  as established by Ghosh fit so well, that we may hope, perhaps, to be able to deduce them from more reasonable assumptions than those of Ghosh. I cannot but think that the right theory of the influence of the interionic forces on the conductivity of ions is still wanting. Of the theories so far proposed, that of Hertz<sup>6</sup> is in my opinion the only reliable one, but it has not been thoroughly worked out.

4. When trying to determine experimentally the value of the activity coefficient  $f_a$  for an ion, various difficulties are encountered.

Firstly, it is difficult to make sure that the electrolyte is *really completely ionized* or, if that is not the case, to determine its degree of dissociation. If the molar conductivity of the electrolyte increases with decreasing concentration according to Ostwald-Walden's valence rule it will, however, be natural, as I have formerly pointed out, to assume complete dissociation. In many cases this point may be investigated by means of spectrophotometric measurements, the colour of the ions being, to a rather high degree, independent of the interionic forces and, on the other hand, greatly influenced by chemical combination of the ions.

Secondly, it is not possible, even if the ion concentration is known, to state with certainty *what the activity of the ion would have been if the interionic forces did not exist*. This difficulty particularly manifests itself in concentrated solutions. As the measure of the activity one should, most likely, take neither the mole number per litre nor the mole number per 1000 g of water but what is known as the mole fraction

$$x = \frac{n}{n + n'}, \quad (12)$$

where  $n$  is the mole number of the solute and  $n'$  the mole number of the solvent. We shall designate this mole fraction as  $x$ -concentration. As to the justification of putting the activity equal to the  $x$ -concentration we may for instance refer to the excellent treatment of ideal solutions in Alex. Findlay's book: *The osmotic pressure*.

Thirdly, *the water content of the ions* in the solution must be considered. When the ions form hydrates in solution the consequence is that the  $x$ -concentrations of the ions will be larger than they would have been without the hydration. This effect of hydration is well known and frequently discussed. There is, however, another effect of hydration which has not as yet been taken into account; although it is rather of greater importance than the former effect. If we want to determine the activity of an ion by means of potential measurements, say with metal or hydrogen electrodes or with mercurous chloride electrodes, we obtain for a hydrated ion by means of the ordinary Nernst formula not a measure of the activity of the ion itself but only of the activity of the ion without water. If the ion contains  $m$   $H_2O$ , we must multiply the activity of the ion, which we may call  $A$ , by the activity of the water to the  $m$ -th power in order to obtain the activity of ion hydrate. We have a good measure of the activity of the water in the vapour pressure of the solution  $p$  divided by the vapour pressure of pure water  $p_0$ . Hence the activity of the actual (hydrated) ion may be written

$$a = A \left( \frac{p}{p_0} \right)^m . \quad (13)$$

Strangely enough, no account has until now been taken of this correction, in spite of the fact that, in the electrometric determination of hydrogen-ion concentration so frequently used recently, it is of considerable magnitude, since the hydrogen ion is very strongly hydrated. The measurement of the potential of a hydrogen electrode in a solution does not directly give us either the hydrogen-ion concentration or the hydrogen-ion activity, but only a fictive quantity which may be designated as the activity of the dehydrated hydrogen ion. Lack of knowledge of this fact has led to the conclusion that the hydrogen-ion activity increases on addition of liberal amounts of neutral salts to hydrochloric and other strong acids (comp. for instance<sup>7</sup>). A similar correction should also be made in the case of activity determinations based on the solubility of salts.

Fourthly, the exact determination of ion activities in concentrated solutions is rendered difficult by the *association of the water*, which is of importance in calculating the  $x$ -concentration, and which is not properly known. In the following this association is, as a rule, left out of consideration. To illustrate the

error thus committed, the calculation is carried through in a single case on the supposition of complete association into double molecules.

5. If the apparent activity coefficient  $F_a$  is defined as the ratio between the activity of the dehydrated ion and the concentration  $c$  expressed in moles per 1000 g of water, and if  $f_a$  is the true activity coefficient taking account of the electric ionic forces, then:

$$F_a \cdot c \cdot \left(\frac{p}{p_0}\right)^m = x \cdot 55.5 \cdot f_a. \quad (14)$$

Both the right and the left side of the equation are expressions for the activity of the ion hydrate. The factor 55.5 arises from the fact that at zero concentration when  $F_a$ ,  $f_a$ , and  $p/p_0$  equal 1, we have

$$c = x \frac{1000}{18.02} = x \cdot 55.5.$$

If we consider a completely dissociated binary electrolyte and call the activity coefficients of the two ions  $F'_a$  and  $F''_a$  and  $f'_a$  and  $f''_a$  respectively and the number of water molecules in the ions  $m'$  and  $m''$ , we get by insertion in equation 14

$$F'_a \cdot c \cdot (p/p_0)^{m'} = \frac{c}{55.5 + 2c - (m' + m'')c} \cdot 55.5 \cdot f'_a \quad (15)$$

$$F''_a \cdot c \cdot (p/p_0)^{m''} = \frac{c}{55.5 + 2c - (m' + m'')c} \cdot 55.5 \cdot f''_a. \quad (16)$$

By logarithmic transformation these expressions give:

$$\ln F'_a + m' \ln p/p_0 = \ln f'_a - \ln \left(1 - \frac{m' + m'' - 2}{55.5} \cdot c\right) \quad (17)$$

$$\ln F''_a + m'' \ln p/p_0 = \ln f''_a - \ln \left(1 - \frac{m' + m'' - 2}{55.5} \cdot c\right). \quad (18)$$

Many of the experimental methods do not determine  $F'_a$  and  $F''_a$  separately but the square root of their product

$$F_a = \sqrt{F'_a \cdot F''_a}. \quad (19)$$

By adding equations 17 and 18, introducing  $F_a$ , and further putting

$$f_a = \sqrt{f'_a \cdot f''_a} \quad \text{and} \quad m = m' + m'', \quad (20)$$

we get

$$\ln F_a + \frac{m}{2} \ln p/p_0 = \ln f_a - \ln \left(1 - \frac{m-2}{55.5} c\right). \quad (21)$$

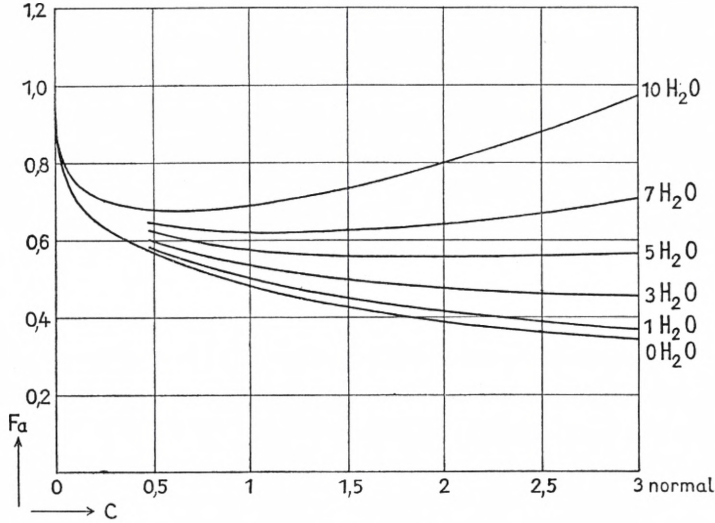


Fig. 1.

This universally valid equation may be simplified by introducing the following approximately valid relations:

$$\ln p/p_0 = -\frac{2c}{55.5} \quad \text{and} \quad -\ln \left(1 - \frac{m-2}{55.5} c\right) = \frac{m-2}{55.5} c, \quad (22)$$

and we get:

$$\ln F_a = \ln f_a + \frac{2m-2}{55.5} c. \quad (23)$$

Fig. 1 gives an impression of the variations of the apparent activity coefficient  $F_a$  for a salt in the case that  $m$  assumes the values 0, 1, 3, 5, 7, 10. In the calculation the assumption  $\log f_a = -0.3 \sqrt[3]{c}$  is made use of. We see that some of these curves show a minimum, and that the concentration at which this minimum is reached is lower the more hydrated the salt is.

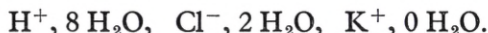
6. At present the degree of hydration of the ions is unknown, and hence it is not possible to use the above equations for the purpose of determining  $f_a$  from measurements of  $F_a$ . Starting from measurements of  $F_a$ , an attempt has been made to calculate the hydration of some electrolytes and ions on the assumption that it is permissible to extend the use of the formula for  $f_a$  applicable to dilute solutions:

$$\ln f_a = -k \sqrt[3]{c}. \quad (24)$$

also to concentrated solutions. A further assumption used below is that the electrolytes are completely ionized.

The calculations themselves give us a certain opportunity of testing the accuracy of our assumptions, as we ought to find a content of water decreasing very slightly with the concentration, or remaining constant. Even if the calculations include solutions up to 4 normal, the activity of water in the solutions will vary only 10 to 20 per cent, which cannot alter the degree of hydration to any extent. In order that a change of the degree of hydration shall take place at all the ion must exist in more than one form in the solution. Supposing, for instance, that at infinite dilution the hydration  $m$  H<sub>2</sub>O results from there being 25 per cent ions with  $(m - 1)$  H<sub>2</sub>O, 50 per cent with  $m$  H<sub>2</sub>O and 25 per cent with  $(m + 1)$  H<sub>2</sub>O, it is easy from the law of mass action to calculate that there will, when the activity of water falls by 20 per cent, be 31 per cent with  $(m - 1)$  H<sub>2</sub>O, 49 per cent with  $m$  H<sub>2</sub>O and 20 per cent with  $(m + 1)$  H<sub>2</sub>O, and the average degree of hydration will have altered only from  $m$  to  $(m - 0.11)$ . The greater the difference in the water contents of the different hydrates existing in the solution, the greater the changes of the average degree of hydration, but the above calculation may serve as an example of the order of magnitude of the effect.

7. The result of the following calculations is that the ions of hydrochloric acid contain about 9 H<sub>2</sub>O and the ions of potassium chloride about 2 H<sub>2</sub>O. A calculation made for the hydrogen ion alone gave 9 H<sub>2</sub>O and for the chloride ion alone 2 H<sub>2</sub>O. Since the sum of these results is 11 H<sub>2</sub>O, while the direct estimation gave 9 H<sub>2</sub>O for the ions of hydrochloric acid, the calculations cannot be quite exact; but this was not to be expected either. According to our calculations the following formulae for the composition of the ions may be used with fair approximation:



If the association of the water is taken into consideration somewhat higher values for the hydration are found. The particulars of the calculations will be given below.

#### THE CALCULATIONS

8. Table 2 contains calculations of the hydration of hydrochloric acid. First column  $c$  gives the concentrations of hydrochloric acid in moles per 1000 g of water; second column,  $F_a$  (Ellis), contains the values of the apparent activity coefficient of the ions of hydrochloric acid as calculated by Ellis<sup>8</sup> from potential measurements. On calculating these values Ellis assumed  $F_a$  in the most dilute solution to equal  $f_a$ . I have preferred to attribute to  $F_a$  in the most dilute solution such a value as to make the formula  $\log F_a = -k \sqrt[3]{c}$ , fit as well as possible for the values of  $c$  below 0.1. In this way I got the values of  $-\log F_a$  given in



the third column. The determination of  $\log p/p_0$  is made from the values of the apparent activity coefficient in the following way.

If the activity of each of the ions of hydrochloric acid were equal to  $c$ , then

$$p/p_0 = e^{-2c/55.5} \quad (25)$$

would apply thermodynamically.

The activity of the ions being  $c \cdot F_a$  a tension coefficient  $F_p$  defined by the following expression may be introduced:

$$p/p_0 = F_p \cdot e^{-2c/55.5}. \quad (26)$$

$F_a$  and  $F_p$  are thermodynamically connected through the equation:

$$2c \frac{d \ln F_a}{dc} + 55.5 \frac{d \ln F_p}{dc} = 0. \quad (27)$$

If  $F_p$  is determined by means of this equation, we shall at once have  $p/p_0$  by means of equation 26.

Starting from Ellis's figures corrected as indicated above, the following interpolation formulae have been established for  $-\log F_a$ :

$$\text{for } c < 0.1: \quad -\log F_a = 0.2 \sqrt[3]{c} \quad (28)$$

$$\text{for } 0.1 < c < 1: \quad -\log F_a = 0.0810 + 0.141 c - 0.138 c^2 \quad (29)$$

$$\text{for } 1 < c: \quad -\log F_a = 0.247 - 0.170 c + 0.0092 c^2 \quad (30)$$

In column 4 (table 2) the corresponding values of  $-\log F_a$  are found. When introducing expressions 28–30 in equation 27, integrating and using 26 the following formulae for  $\log p/p_0$  are obtained:

$$\text{for } c < 0.1: \quad -\log p/p_0 = 0.01566 c (1 - 0.115 \sqrt[3]{c}) \quad (31)$$

$$\text{for } 0.1 < c < 1: \quad -\log p/p_0 = 0.01566 c (1 - 0.161 c + 0.212 c^2) - 0.00006 \quad (32)$$

$$\text{for } 1 < c: \quad -\log p/p_0 = 0.01566 c (1 + 0.196 c - 0.0141 c^2) - 0.0022 \quad (33)$$

The values of  $-\log p/p_0$  calculated by means of these formulae are given in column 5. In column 6 are given the values of  $-\log f_a$  calculated according to

the formula  $-\log f_a = 0.2 \sqrt[3]{c}$ . According to expression 28 this formula applies to  $f_a$  at low concentrations since in this case we may put  $f_a = F_a$ , and we shall suppose that the same formula may be used at high concentrations. Finally, column 7 shows  $m$ , the number of  $\text{H}_2\text{O}$  which, according to equation 21, must be bound to the ions of hydrochloric acid. It will be seen that the average number of bound water molecules is 9. Thus the hydrogen ion and the chloride ion bind 9  $\text{H}_2\text{O}$  in all.

Table 2. Hydration of hydrochloric acid according to activity measurements by Ellis at 25° C.

$c$	$F_a$ (Ellis)	$-\log F_a$	$-\log F_a$ calc.	$-\log p/p_o$	$-\log f_a$	$m$
0.00168	0.988	0.0238	0.0238			
0.002	0.987	0.0242	0.0252			
0.005	0.971	0.0313	0.0342			
0.01	0.947	0.0422	0.0430			
0.02	0.918	0.0557	0.0542			
0.05	0.874	0.0770	0.0736			
0.10	0.843	0.0927	0.0930			
0.20	0.818	0.1057	0.1037			
0.30	0.804	0.1132	0.1132			
0.50	0.793	0.1192	0.1170	0.00756	0.159	8.5
0.75	0.820	0.1047	0.1090	0.01168	0.182	9.0
1.00	0.857	0.086	0.086	0.01634	0.200	9.0
2.00	1.186	-0.056	-0.057	0.0398	0.252	9.5
4.484	2.228	-0.329	-0.329	0.1098	0.330	7.6
						mean 8.7

9. In order to determine the *hydration of potassium chloride* we must proceed in another way since the apparent activity coefficient of the ions in this salt has not been measured. The hydration is calculated from the freezing point lowering of potassium chloride. Determinations of freezing points give us the activity of water and, as this will allow us to calculate thermodynamically the apparent activity of the ions, the possibility of such calculations follows from the above considerations. It is true that Jones and Biltz have long ago determined the hydration of electrolytes, starting from determinations of freezing points, but their procedure was rather inexact. The following method is better: Starting from the expression

$$Q = 18.02 (79.65 - 0.53t) \quad (34)$$

in which  $Q$  is the heat of fusion of ice and  $t$  the freezing point lowering, we obtain by integration of the equation

$$\frac{d \ln p/p_o}{dt} = - \frac{Q}{R (273.1 - t)^2} \quad (35)$$

the following formula for  $\log p/p_o$

$$\log p/p_o = - 0.00421 \cdot t \cdot (1 + 0.00033 t). \quad (36)$$

In the case of an ideal solution of neutral molecules we have:

$$p/p_o = 1 - x. \quad (37)$$

In the case of an ideal solution of ions we may put:

$$p/p_o = (1 - x)f_p. \quad (38)$$

Here  $f_p$  is the tension coefficient due to the interionic electric forces.  $f_p$  is thermodynamically connected with  $f_a$  by the following relation:

$$x \frac{d \ln f_a}{dx} + (1 - x) \frac{d \ln f_p}{dx} = 0. \quad (39)$$

If  $\ln f_a = -k \sqrt[3]{x}$  we obtain by integration:

$$\ln f_p = \frac{k}{4} x^{\frac{4}{3}} \left( 1 + \frac{4}{7} x + \frac{4}{10} x^2 + \dots \right). \quad (40)$$

For the ions of the potassium chloride we may put  $\log f_a = -0.25 \sqrt[3]{c}$ ; by introducing  $c = x \cdot 55.5/2$  and by discarding higher powers of  $x$  in equation 40 we have:

$$\log f_p = 0.00225 c^{\frac{4}{3}}. \quad (41)$$

From the equations 36, 38, and 41 we obtain:

$$-\log(1 - x) = 0.00421 (1 + 0.00033 t) t + 0.00225 \cdot c^{\frac{4}{3}}. \quad (42)$$

If  $x$  is calculated by means of this equation,  $m$ , the number of  $\text{H}_2\text{O}$  bound to the ions of potassium chloride, may be obtained from the equation

$$x = \frac{2c}{55.5 + 2c - mc} \quad (43)$$

giving

$$m = 2 + \frac{55.5}{c} - \frac{2}{x}. \quad (44)$$

Table 3 contains the results of such a calculation.

Table 3. Hydration of potassium chloride according to determinations of freezing points

$c$	$t^*$	$x$	$m$
0.339	1.130	0.01212	(1.0)
0.428	1.404	0.01529	(-0.2)
0.476	1.605	0.01755	(3.7)
0.704	2.283	0.02503	0.9
0.772	2.529	0.02821	2.1
1.00	3.286	0.03640	2.5
1.03	3.37	0.03811	3.4
1.989	6.46	0.07295	2.5
3.269	10.61	0.1204	2.4
			mean 2.3

\* Values taken from Landolt-Börnstein's tables.

The values for  $m$  in the most dilute solutions vary greatly; but it is also seen from formula 44 that a small error in the determination of  $c$  or  $t$  will have an influence on  $m$  that will be greater the more dilute the solution. On calculating a mean value of  $m$  leaving out the results for the three most dilute solutions, we obtain  $m = 2.3$ . According to this potassium chloride contains about 2 H<sub>2</sub>O.

10. Table 4 shows the results of a calculation of the hydration of hydrochloric acid from determinations of the freezing points. We assume that  $f_a$  for the ions of hydrochloric acid at the freezing point is determined by  $-\log f_a = 0.25 \sqrt[3]{c}$ . According to Milner's theory  $-\log f_a$  at the freezing point should be greater than at 25° C, where we used  $-\log f_a = 0.20 \sqrt[3]{c}$ . The calculation gives as a mean  $m = 7.9$ . This is somewhat less than calculated above from Ellis's activity measurements ( $m = 8.7$ ). Since experimental errors no doubt exert a greater influence on the calculation based on determinations of freezing points than on that based on measurements of activity, I attach little importance to the smaller value.

Table 4. Hydration of hydrochloric acid according to determinations of freezing points

$c$	$t$	$x$	$m$	$m$ for $\log f_a =$ $-0.20 \sqrt[3]{c}$	$m$ for $t$ 1 % greater	$m$ for (H <sub>2</sub> O) <sub>2</sub>
0.2443	0.888	0.00936	(15.6)	(12.0)	(20.0)	(16.8)
0.4598	1.67	0.01789	(10.9)	(8.6)	(13.1)	(11.6)
1.017	4.04	0.04356	10.7	9.5	11.6	11.6
1.563	6.57	0.07061	9.2	8.4	9.7	10.1
3.052	14.97	0.1546	7.2	6.9	7.5	7.9
4.064	23.05	0.2253	6.8	6.5	7.0	7.2
4.656	28.84	0.2704	6.5	6.3	6.7	6.8
			mean 7.9	7.5	8.5	8.7

In order to be able to evaluate the assumptions made in the calculation of  $m$ , we give in table 4 values of  $m$  which are calculated on somewhat altered assumptions, viz, that  $\log f_a = -0.20 \sqrt[3]{c}$  instead of  $-0.25 \sqrt[3]{c}$ , that  $t$  is 1 per cent greater, and that all molecules of water are associated to (H<sub>2</sub>O)<sub>2</sub>. In none of these cases the mean value of  $m$  will change by more than 0.8.

The calculation of  $m$  for water associated to (H<sub>2</sub>O)<sub>2</sub> is undertaken in the following way. As the water consists of double molecules (H<sub>2</sub>O)<sub>2</sub> and the vapour consists of single molecules we have:

$$p/p_o = \sqrt{1 - x f_p}. \quad (45)$$

By combination with equations 36 and 41 this expression gives:

$$-\log(1-x) = 2(0.00421 t(1 + 0.00033 t) + 0.00225 c^{\frac{4}{3}}). \quad (46)$$

When  $x$  is determined by this equation,  $m$  is obtained from the equation

$$x = \frac{2c}{27.75 + 2c - \frac{m}{2}c} \quad (47)$$

which gives

$$m = 4 + \frac{55.5}{c} - \frac{4}{x}. \quad (48)$$

11. As yet only the *total* hydration of electrolytes has been calculated. It is, however, possible to calculate the hydration of the *single* ions if only the apparent activity coefficients of the single ions are known. These can be determined by means of measurements of the e.m.f. of cells of the following types:

metal/salt-solution I/salt-solution II/metal.

The difficulty in calculating the activity from such measurements lies in the elimination of the diffusion potential between the solutions. The calculation of the hydration of the hydrogen ion is made by means of Harned's<sup>7</sup> measurements of cells of the type:

Hg/HgCl, 1 M KCl/saturated KCl/ $c$  M KCl in 0.1 M HCl/H<sub>2</sub>.

Harned eliminated the diffusion potential between saturated KCl and  $c$  M KCl in 0.1 M HCl by an empiric and, in my opinion, unwarranted method. I have preferred to calculate the diffusion potential according to Henderson's formula. If  $E$  is the electrode potential corrected for the diffusion potential and  $E_0$  the value of this potential for  $c = 0$  (hydrochloric acid without potassium chloride) the following equation serves for the determination of the apparent activity coefficient  $F_a$  of the hydrogen ion,

$$\log F_a - \log [F_a]_0 = (E_0 - E)/0.0591. \quad (49)$$

Here  $[F_a]_0$  is the value of the activity coefficient in hydrochloric acid without potassium chloride.

If we consider a solution containing  $c_1$  moles of HCl and  $c_2$  moles of KCl per 1000 g of H<sub>2</sub>O, and if we suppose that the ions of the hydrochloric acid contain 9 H<sub>2</sub>O and the ions of the potassium chloride 2 H<sub>2</sub>O as found above, we have the following equation:

$$F_a \cdot c_1 \cdot (p/p_0)^m = c_1 \cdot \frac{55.5}{55.5 + 2c_1 + 2c_2 - 9c_1 - 2c_2} \cdot f_a. \quad (50)$$

Here  $F_a$  is the apparent activity coefficient of the hydrogen ion,  $f_a$  the activity coefficient originating from the interionic electric forces and  $m$  the number of water molecules in the hydrogen ion. Both right and left sides of the equation express the activity of the hydrogen-ion hydrate. From equation 50 we easily get:

$$\log F_a + m \log p/p_o = \log f_a - \log \left(1 - \frac{7c_1}{55.5}\right). \quad (51)$$

Applied to the solution of hydrochloric acid without potassium chloride, equation 51 gives

$$\log [F_a]_o + m \log [p/p_o]_o = \log [f_a]_o - \log \left(1 - \frac{7c_1}{55.5}\right). \quad (52)$$

By subtraction of equation 52 from 51 and isolation of  $m$  we get:

$$m = \frac{\log F_a - \log [F_a]_o - \log f_a + \log [f_a]_o}{\log [p/p_o]_o - \log p/p_o}. \quad (53)$$

From this equation  $m$  is calculated.  $\log F_a - \log [F_a]_o$  is obtained by means of formula 49 from Harned's potential measurements. For the calculation of  $\log f_a$  and  $\log [f_a]_o$  the following formula is used:

$$\log f_a = -0.2 \sqrt[3]{c_1 + c_2}; \quad (54)$$

$\log p/p_o$  and  $\log [p/p_o]_o$  are calculated from the freezing points of the solutions by means of equation 36. By the latter calculation it is assumed that a solution with the concentrations 0.1 M HCl and  $c$  M KCl freezes at the same temperature as a  $(c + 0.1)$  M KCl solution. Table 5 shows the results of the calculation.

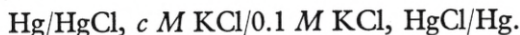
Table 5. Hydration of the hydrogen ion according to activity measurements at 25° C.

$c$	$c_1$	$c_2$	$E$	Diff.- potential	$\log F_a$ $-\log [F_a]_o$	$-\log f_a$	$-\log p/p_o$	$m$
0	0.1004	0	0.3495	0.0048		0.093	0.0015	
1.100	0.1004	1.143	0.3459	0.0024	0.020	0.212	0.0172	8.9
1.376	0.1004	1.441	0.3443	0.0022	0.044	0.238	0.0212	9.6
3.134	0.1004	3.474	0.3326	0.0014	0.229	0.296	0.0492	9.1
								mean 9.2

Harned makes up his solution by dissolving  $c$  moles of KCl in 1 litre of 0.1 M HCl. The values of  $c$  are given in column 1; in columns 2 and 3,  $c_1$  and  $c_2$ , the numbers of moles of HCl and KCl per 1000 g of H<sub>2</sub>O are given, calculated from  $c$  on the assumption that the apparent molar volumes are 18 cc. for HCl and 30 cc. for KCl. Column 4,  $E$ , gives the potentials as found by Harned; column 5 the diffusion

potentials calculated according to Henderson (*cf.* Bjerrum<sup>9</sup>); column 6 the values of  $\log F_a - \log [F_a]_0$  calculated according to formula 49; column 7 —  $\log f_a$  calculated from expression 54, and column 8 —  $\log p/p_0$  calculated according to formula 36. Finally in the last column the values of  $m$  calculated according to formula 53 are shown. The mean value of  $m$ , 9.2, shows that the greater part of the water bound by the ions of hydrochloric acid, must be ascribed to the hydrogen ion.

12. For the determination of the hydration of the chloride ion Harned's potential measurements with cells of the following type may be used:



From these measurements Harned rightly eliminated the diffusion potential by means of Nernst's formula. For the determination of the apparent activity coefficient of the chloride ion we have

$$\log [F_a]_{c_1} - \log [F_a]_{c_1'} = \frac{E}{0.0591} \log \frac{c_1}{c_1'} \quad (55)$$

Here  $c_1$  and  $c_1'$  indicate the concentrations of the solutions used in moles of KCl per 1000 g of  $\text{H}_2\text{O}$ , and  $E$  is the potential corrected for the diffusion potential. The calculation of  $m$  for the chloride ion may be made according to the same formula 53 as used in the case of the hydrogen ion. Table 6 contains the results of the calculations.

Table 6. Hydration of the chloride ion according to activity measurements at 25° C.

$c$	$c_2$	$E$ corr. for Diff.-Pot.	$\log [F_a]_0$ — $\log [F_a]_{0.1}$	— $\log f_a$	— $\log p/p_0$	$m$
0.1	0.1005	0	0	0.116	0.0014	—
1.0	1.038	0.05340	— 0.109	0.250	0.0143	1.9
1.9	2.020	0.06912	— 0.133	0.310	0.0276	2.3
3.1	3.427	0.08247	— 0.136	0.364	0.0468	2.5
						mean 2.2

In column 1,  $c$ , the molar concentrations of potassium chloride (moles per litre) are given according to Harned. Column 2 shows the values of  $c_2$ , the concentration of potassium chloride in moles per 1000 g of water. In this calculation of  $c_2$  the apparent molar volume in the solution of potassium chloride is put equal to 30 cc. Column 3 contains the results of Harned's potential measurements corrected for the diffusion potential. Column 4 contains the values of  $\log [F_a]_c - \log [F_a]_{0.1}$ , calculated by means of eq. 55; column 5 the values of —  $\log f_a$  calculated from the expression  $0.25 \sqrt[3]{c}$ ; column 6 the values of —  $\log p/p_0$  calculated from deter-

minations of freezing points according to formula 36. Finally the last column contains the values of  $m$  calculated according to formula 53. The mean value is 2.2 and hence the formula for the chloride ion must be supposed to be  $\text{Cl}^-$ ,  $2\text{H}_2\text{O}$ .

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