CCCXV.—*The Calculation of Activity Coefficients from Solubility Measurements. Part II. Thallous Iodate.*

By Cecil Whitfield Davies.

In Part I (Blayden and Davies, this vol., p. 949) it was pointed out that in calculating the activity coefficients of a sparingly soluble salt from its solubility in the presence of other salts, allowance must be made for the incomplete dissociation of both the saturating and the added salt. It was shown that when the necessary corrections are applied to the published results for thallous chloride, the data for this salt in dilute salt solutions reveal new regularities. The activity coefficient is, within experimental error, the same in any solution of the same ionic strength and is independent of the nature of the added salt. It was also shown that this new relationship provides a method of finding the extent of dissociation of any soluble salt. In view of the interest and potential value of these results it seems desirable to extend the calculations to other data. For this purpose the recent results of LaMer and Goldman (*J. Amer. Chem. Soc.*, 1929, **51**, 2632) for thallous iodate at 25° are particularly suitable, for they extend to lower concentrations than do the data for thallous chloride, and at the same time appear to be more accurate.

Determination of the Solubility Product.—The solubility of thallous iodate at 25° is reported as 0·001844 g.-mol. per litre, individual determinations differing from one another by not more than 0·4%. The dissociation constant of the salt is unknown, but it is evident from the low solubility that the correction for undissociated thallous iodate will be very small. It can be found with quite sufficient accuracy by analogy with those thallous salts for which dissociation constants are known. These are the nitrate, $K = 0{\cdot}56$ (Davies, *Trans. Faraday Soc.*, 1927, **23**, 354); chloride, $K = 0{\cdot}284$ (Part I, *loc. cit.*); and chlorate, $K = 0{\cdot}34$ (*idem, ibid.*). If we take $K = 0{\cdot}5$ for thallous iodate, we find the concentration of undissociated salt to be 5×10^{-6} g.-mol. per litre, and the concentration of the ions to be $1{\cdot}839 \times 10^{-3}$ g.-mol. per litre.

Solubilities in the Presence of Sodium and Potassium Chlorides and Nitrates.—The methods of calculation are similar to those described in Part I. The figures for each solubility measurement have to be corrected for the undissociated parts of the salts present. Thus, the saturated solution in the presence of potassium nitrate contains undissociated thallous and potassium iodates as well as thallous and potassium nitrates. The concentration of undissociated thallous iodate is always taken as 5×10^{-6} g.-mol. per litre, for the addition of other salts cannot affect this to a significant extent. To calculate the concentrations of the others, use must be made of the mass-action expression, $K = f_{\pm}^2 C_C C_A / C_{CA}$ (where C_C, C_A, and C_{CA} are the concentrations of kation, anion, and undissociated salt, and $f_{\pm}$ is the mean ion-activity coefficient), and it is necessary to know the value of K and the value, in each mixture, of $f_{\pm}$. The dissociation constants used are as follows (Davies, *loc. cit.*):

KIO_3.	$NaIO_3$.	KCl.	NaCl.	TlCl.	KNO_3.	$NaNO_3$.	$TlNO_3$.
2·00	3·00	∞	∞	0·284	1·37	3·86	0·56

The values of $f_{\pm}$ appropriate to the mixtures considered are not known, and cannot be calculated on theoretical grounds. It is known, however, that the activity coefficient–concentration curves of all uni-univalent salts lie very close together from infinite dilution up to the highest concentrations here considered—about 0·1N;

TABLE I.

m.	s.	μ.	$\sqrt{\mu}$.	log $I.C.P.$	$-\log f$.	$D\,.\,10^3$ (C.W.D.).	$D\,.\,10^3$ (L. & G.).
Water.							
—	0·001844	0·001839	0·0429	−5·4708	0·0198	0·0	—
Potassium Chloride.							
0·01	0·002005	0·01194	0·1093	−5·4116	0·0494	+0·6	+ 2·7
0·02	0·002107	0·02198	0·1482	−5·3801	0·0651	+0·2	+ 4·5
0·05	0·002335	0·05208	0·2282	−5·3191	0·0956	−0·2	+ 8·7
0·10	0·002625	0·10212	0·3195	−5·2537	0·1283	+0·6	+13·3
Sodium Chloride.							
0·10	0·002620	0·10214	0·3196	−5·2505	0·1299	+2·2	+12·4
Potassium Nitrate.							
0·01	0·001987	0·01189	0·1090	−5·4137	0·0483	−0·3	− 1·2
0·02	0·002079	0·02179	0·1476	−5·3807	0·0648	+0·2	− 1·2
0·05	0·002270	0·05097	0·2258	−5·3209	0·0947	−0·2	− 3·5
0·10	0·002492	0·09836	0·3136	−5·2609	0·1247	−0·9	− 9·2
Sodium Nitrate.							
0·10	0·002486	0·10078	0·3174	−5·2599	0·1252	−1·8	−10·3
Potassium Sulphate.							
0·001	0·001912	0·00483	0·0695	−5·4462	0·0321	+0·5	+ 2·0
0·002	0·001958	0·00777	0·0882	−5·4312	0·0396	−0·2	+ 2·6
0·005	0·002075	0·01647	0·1284	−5·3948	0·0578	+1·0	+ 7·0
0·01	0·002193	0·03058	0·1749	−5·3619	0·0742	−1·3	+ 6·4
0·013	0·002252	0·03898	0·1974	−5·3466	0·0819	−2·3	+ 5·9
0·03	0·002513	0·08530	0·2921	−5·2802	0·1151	−3·4	+ 2·5
0·03333	0·002544	0·09423	0·3070	−5·2737	0·1183	−5·3	− 0·2
0·05	0·002747	0·1383	0·3719	−5·2237	0·1433	−1·1	− 2·5
0·05	*0·002747*	*0·1381*	*0·3716*	*−5·2498*	*0·1303*	—	—
Sodium Sulphate.							
0·03333	0·002543	0·09550	0·3090	−5·2769	0·1167	−7·5	− 0·4
0·05	0·002740	0·1410	0·3755	−5·2303	0·1400	−5·5	− 3·6
0·05	*0·002740*	*0·1401*	*0·3742*	*−5·2517*	*0·1293*	—	—

and it has therefore been assumed that in each solution $f_{\pm}$ has the same value for the other salts present as it has for the thallous iodate itself. This value, and the concentrations of the various species present, are found by a method of successive approximations.

It may seem quite unsound that the activity coefficients reported for thallous iodate should be founded on assumptions regarding the activity coefficients of the other salts present; but these assumptions are involved only in small correction terms, and it can easily be proved that no plausible alteration in the activity coefficient taken for the solvent salt could materially affect the results.

The results are in Table I. The first column shows the concentration of added salt, and the second the solubility of thallous iodate, both in g.-mols. per litre; the third column shows the ionic strength (per litre), the fourth the square root of this quantity, and the fifth the logarithm of the product of the concentrations of the thallous and iodate ions. The remaining columns of Table I are discussed later.

Solubilities in the Presence of Sodium and Potassium Sulphates.— The dissociation of sodium, potassium, and thallous sulphates has recently been examined (Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592). In dilute solutions the numbers of electrically neutral molecules are negligible, and the first stage in the association of the ions ($M^{\cdot} + SO_4'' \rightleftharpoons MSO_4'$) can be expressed with the aid of the mass-action equation :

$$K = \frac{f_{M}f_{SO_4}}{f_{MSO_4}} \cdot \frac{m_{M}m_{SO_4}}{m_{MSO_4}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where f is the activity coefficient and m the molar concentration of an ion. The activity coefficient of an ion can be represented by the equation :

$$\log f = -Az^2\sqrt{\mu} + B\mu \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where z is the valency of the ion, μ is the ionic strength, A is (theoretically) a universal constant, and B is another constant depending on the nature of the ions present. Equation (1) can therefore be put in the form :

$$\log m_{M}m_{SO_4}/m_{MSO_4} = \log K + \Sigma Az^2\sqrt{\mu} - \Sigma B\mu \quad . \quad . \quad (3)$$

and equation (3) is valid for the three salts here considered, the constants having the values :

	K.	ΣAz^2.	ΣB.
Na_2SO_4	0·198	2·0	1·30
K_2SO_4	0·151	2·0	1·05
Tl_2SO_4	0·0472	2·0	1·99

By using these values, the composition of sodium or potassium sulphate solutions saturated with thallous iodate can be calculated. The amount of undissociated uni-univalent salt (sodium or potassium iodate) is calculated as before from the known dissociation constant and the assumption that the activity coefficient is the same as for thallous iodate itself, whilst the concentrations of the intermediate ions, $TlSO_4'$ and $NaSO_4'$ or KSO_4', are found from the values of K, A, and B just tabulated. At this stage a difficulty enters into the calculation which was not present with the chlorides and nitrates. With the uni-univalent salt mixtures it was quite sufficiently accurate to assume a common activity coefficient value for all the salts present in a solution of low ionic strength; but with multivalent electrolytes the activity coefficient changes much more rapidly with changing concentration, and an accurate knowledge of its true value is essential to the calculations. Now the activity constants tabulated for the thallous sulphate ions, *viz.*, $\Sigma A = 2{\cdot}0$ and $\Sigma B = 1{\cdot}99$, were determined for pure thallous sulphate solutions; in a solution which is predominantly potassium sulphate this ΣB value will not apply. Since $\Sigma B = B_{\mathrm{SO_4''}} + B_{\mathrm{Tl^{\cdot}}} - B_{\mathrm{TlSO_4'}}$ (and in the summation the $B_{\mathrm{SO_4''}}$ term will predominate), and since the solution is practically one of potassium sulphate, it is more reasonable to take the value $\Sigma B = 1{\cdot}05$ in calculating the amount of the $\mathrm{TlSO_4'}$ ion as well as that of the $\mathrm{KSO_4'}$ ion present. The calculation has been made on this basis; similarly, in the sodium sulphate solutions the value $\Sigma B = 1{\cdot}30$ has been used in calculating the concentrations of both $\mathrm{NaSO_4'}$ and $\mathrm{TlSO_4'}$. The results obtained in this way are shown in ordinary type in Table I.

In the present state of our knowledge of activity coefficients in mixtures, it will be a matter of opinion as to whether this method of calculation is the best one. The calculations have therefore been repeated using the value $\Sigma B = 1{\cdot}99$ in deriving the concentrations of thallosulphate ion, and the results at the highest concentrations are shown in italics in Table I; at ionic strengths less than 0·04, the precise value of ΣB is of no importance, while at higher concentrations the correct figures will probably lie between those obtained by these two methods.

Discussion of Results.

On the Debye–Hückel theory the activity coefficient of an ion is given by

$$-\log f = Az^2\sqrt{\mu}/(1 + a\sqrt{\mu})$$

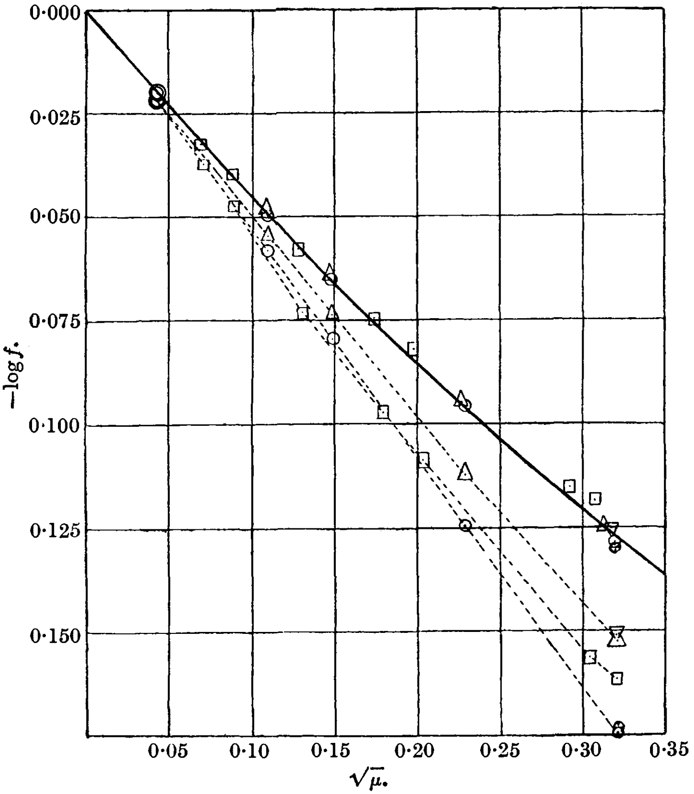
or by

$$-\log f = Az^2\sqrt{\mu} - B\mu$$

where A, B, and a are constants. The second of these is the more convenient in practice and is adopted here. Now, before the ionic equilibria in a mixture of electrolytes can be elucidated, and the composition and behaviour of the mixture thereby determined, both the dissociation constant and the activity coefficient must be known for each electrolyte added, or formed by double decomposition. The dissociation constants can always be found from conductivities and sometimes by other methods (compare Davies; Blayden and Davies; and Righellato and Davies, *locc. cit.*); it is largely in the hope of contributing to a solution of the second part of the problem that the present series of papers is being written. We require to know, therefore, what values for A and B best fit the corrected experimental results of Table I, and to what extent these values are affected by the nature of the added salt.

Dependence on the Nature of the Added Salt.—In their original treatment of the data, LaMer and Goldman followed the usual custom of assuming the salts employed to be completely dissociated. On this basis the solubility of the thallous iodate is inversely proportional to its mean activity coefficient, and, combining this with the limiting relationship, $-\log f = A\sqrt{\mu}$, the authors plotted the logarithm of the solubility against the square root of the ionic strength. By a short extrapolation to $\mu = 0$, they were thus enabled to calculate the activity coefficients of thallous iodate in the various salt solutions, and they then compared these values with the limiting theoretical equation of Debye and Hückel, *viz.*, $-\log f = 0{\cdot}505\sqrt{\mu}$. Their differences, $\log f\,(\text{obs.}) - \log f\,(\text{calc.})$,

FIG. 1.



Activity coefficients of thallous iodate in the presence of: KCl ⊙; NaCl ⊕ KNO_3 △; $NaNO_3$ ▽; K_2SO_4 ⊡. *Broken lines show the curves of LaMer and Goldman. The full line is drawn through the corrected points.*

are reproduced in col. 8 of Table I. A value of $D \times 10^3 = 1{\cdot}0$ would be accounted for by experimental error, if the maximum error in the mean solubility results be taken as 0·1%. Their results are also shown by dotted curves in Fig. 1.

The results are typical of those obtained in this way for the activity coefficients of sparingly soluble salts. The deviations from uniform behaviour are large and follow no general rule; they are positive for the chlorides and negative for the nitrates, while the complete curve for potassium sulphate shows a "hump," the deviations being first positive and then negative.

To recalculate the activity coefficients with allowance for incomplete dissociation, it will be evident that LaMer and Goldman's method must be modified by employing corrected figures for the ionic strength, and by using the square roots of the ion-concentration products (*I.C.P.*), from col. 5 of Table I, in place of the total solubility; the limiting value of log *I.C.P.*, found by extrapolation, is $-5{\cdot}5103$. The corrected figures for $-\log f$ are plotted against $\sqrt{\mu}$ in Fig. 1. They are also shown in col. 6 of Table I, and in col. 7 they are compared with values calculated from the equation

$$-\log f = 0{\cdot}470\sqrt{\mu} - 0{\cdot}22\mu \quad . \quad . \quad . \quad . \quad (4)$$

On comparing col. 7 of Table I with col. 8, it will be seen that the corrections for incomplete dissociation entirely remove the anomaly, reported by LaMer and Goldman, that the activity coefficient of the thallous iodate is dependent on the nature of the added salt even at the lowest ionic strengths. Instead, the results at low ionic strengths are in perfect agreement with the common equation (4); specific influences do not become appreciable, among uni-univalent salts, at concentrations less than $N/10$, while with the sulphate solutions and, presumably, with other multivalent electrolytes the specific character of the B term becomes of importance at about half this concentration. If the three series, for potassium chloride, potassium nitrate, and potassium sulphate, are considered separately, each leads to a value 0·47 for the A coefficient of equation (2), while, for complete agreement between the equation and experiment, B must be given the value 0·21 for potassium chloride as added salt, 0·23 for potassium nitrate, and a value between 0·27 and 0·34 for potassium sulphate, the latter value being required by the italicised figures of Table I.

The results therefore confirm the conclusions already reached in Part I, and again bring solubility measurements into agreement with the theory of the subject.

The Value of the Factor A.—On the Debye–Hückel theory, A is a universal constant which has the value 0·50 for aqueous solutions at 25°. If true, this universal value would be extremely convenient; it has been adopted by Brönsted, for instance, in his treatment of the kinetics of reactions in solutions, and its simplicity has materially helped in the development of that subject. Moreover, it would open the way to a straightforward experimental study of the B factor in mixed electrolytes and to the formulation of rules concerning its dependence on composition. Unfortunately, the value $A = 0{\cdot}50$ does not seem to be borne out by experiment, and it is doubtful whether its acceptance, as sufficiently accurate for most purposes, is justified. Rather, it seems needful at present to determine A wherever possible by experiment.

In Part I it was pointed out that for several organic acids and for hydrochloric acid A has the value 0·39; and that for the common uni-univalent salts A. A. Noyes adopted the value $A = 0{\cdot}41$. It was then shown that the corrected activity coefficients of thallous chloride in the presence of potassium chloride are given by the equation $-\log f = 0{\cdot}38\sqrt{\mu}$, and that the other available series of measurements for thallous chloride agree with this at low concentrations. In applying this simple equation, however, the slight curvature of the $\log f$–$\sqrt{\mu}$ curves was ignored. Actually, if each series is fitted separately to equation (2), the results for thallous chloride are as follows :

Solvent salt.	KCl.	HCl.	$BaCl_2$.	$TlNO_3$.	HNO_3.
A	0·39	0·42	0·42	0·40	0·42
B	0·04	0·21	0·16	0·10	0·22

The mean value for thallous chloride therefore is $A = 0{\cdot}41$. For thallous iodate we now find the value $A = 0{\cdot}47$. It therefore seems necessary to conclude, if the form of equation (2) is accepted for ionic strengths up to 0·1, not only that A has usually a value much lower than the Debye–Hückel value, but that it varies from salt to salt. The unusually high value for thallous iodate recalls the fact discovered many years ago (see Lewis and Randall, "Thermodynamics," 1923, p. 344) that sodium and potassium iodates have, in dilute solutions, markedly lower activity coefficients than have the other common uni-univalent salts. A high A value would therefore appear to be an attribute of the iodate ion.

The Principle of Specific Interaction.—The "Principle of the Specific Interaction of Ions" was framed by Brönsted (*J. Amer. Chem. Soc.*, 1922, **44**, 877; 1923, **45**, 2898) to account for the deviations from ideal behaviour encountered in studying activity coefficients in salt mixtures. Its underlying idea can be outlined as follows. In a mixture of two salts, AB and XY, the activity coefficient of AB is mainly determined (as in the Debye–Hückel limiting equation) by the ionic strength of the solution. But the electrical interaction will to some extent be affected by the nature and configuration of the ions present, and this specific influence of XY on the activity coefficient of AB will, in dilute solutions, be due only to the influence of the anion Y on the kation A and of X on B, for the ions of like sign are always at too great distances to exert specific effects. A consequence of this is that the ratio of the activity coefficient of AB in, say, a nitrate solution to its activity coefficient in a chloride solution with the same kation and of the same concentration should be the same whatever the kation may be. This principle is supported by the numerous solubility measurements of Brönsted himself (*loc. cit.*), and by the accurate measurements of Güntelberg (*Z. physikal. Chem.*, 1926, **123**, 199). Further, it is stated by LaMer and Goldman (*loc. cit.*) that the principle is confirmed by the solubility relationships of thallous iodate and thallous chloride.

The bearing on this statement of the calculations given in the present paper and in Part I will be evident. When allowance is made for incomplete dissociation, the specific deviations, with both thallous chloride and iodate, practically vanish. The constant solubility ratios found by LaMer and Goldman for, say, thallous iodate in nitrate and chloride solutions are wholly due to the formation of undissociated thallous nitrate in the one series of measurements and the formation of thallous chloride, with its markedly different dissociation constant, in the other; they in no way reflect a specific electrical interaction in Brönsted's sense between the thallous ion and the two anions.

It would seem probable that much of Brönsted's own experimental support for the principle is open to similar objections, though this cannot be tested through lack of the necessary dissociation data. At the same time it should be noted that this criticism is not levelled at the principle itself; it robs it of much of its experimental support, but on the other hand Güntelberg's results were obtained with salts which we consider completely dissociated and they are therefore outside the scope of the criticism.

Solubilities in the Presence of Magnesium Chloride and Nitrate.—LaMer and Goldman also measured the solubility of thallous iodate in magnesium chloride and nitrate solutions. They found anomalies similar to those already discussed; that is, the solubilities are far greater in magnesium chloride than in magnesium nitrate solutions of the same concentration. Evidently the same explanation as before will apply: a larger amount of the thallous ion is removed by double decomposition in the first case than in the second. The results cannot be treated in the same way as the previous ones, since the bivalent magnesium ion will presumably react to some extent to form the $MgIO_3^{\cdot}$ ion, and the extent of dissociation of this is unknown. Instead, we may make use of the results to calculate the dissociation constant of the $MgIO_3^{\cdot}$ ion, as follows.

In the solutions already considered, specific deviations were found to be only small among isotypic salts, so that the activity coefficient of thallous iodate in any uni-bivalent salt solution will be very nearly the same as in a potassium or sodium sulphate solution of the same ionic strength. The activity coefficient of thallous iodate in magnesium chloride or nitrate solutions will therefore almost certainly lie between the extreme values given for the sulphate solutions; that is, it will be given by the equation $\log f = -0{\cdot}47\sqrt{\mu} + B\mu$, where B has a value between 0·27 and 0·34. The calculations that follow have been carried out using these two values in turn.

Magnesium chloride and nitrate are both completely dissociated (Righellato and Davies, *loc. cit.*), so that the thallous iodate–magnesium salt mixtures contain, besides the simple ions, only undissociated thallous iodate, undissociated thallous chloride or nitrate, and the $MgIO_3^{\cdot}$ ion. The concentration of undissociated thallous iodate is always 0·005 millimol. per litre as before. The concentrations of the other species are determined by successive approximations; a plausible value is first given to the concentration of undissociated thallous chloride or nitrate, and this determines the concentration of thallous ion which then gives, from the solubility-product principle, the concentration of iodate ion; the concentration of the $MgIO_3^{\cdot}$ ion is now found by subtraction, and hence a closer approximation to the true ionic strength and true concentrations is obtained, and so on until final agreement is reached. The results of the calculation, using the two values for B, are shown in Table II. The first column shows the solvent salt and the second its molar concentration. The third and sixth give the ionic strength, on the two bases of calculation, the fourth and seventh give the concentration of $MgIO_3^{\cdot}$ ion in millimols. per litre, and the fifth and eighth give the logarithm of the "classical" dissociation constant of the $MgIO_3^{\cdot}$ ion: $k' = m_{Mg} . m_{IO_3}/m_{MgIO_3}$.

TABLE II.

		$B = 0{\cdot}27$.			$B = 0{\cdot}34$.		
Salt.	m.	μ.	$MgIO_3^{\cdot}$.	$\log k'$.	μ.	$MgIO_3^{\cdot}$.	$\log k'$.
$MgCl_2$	0·03333	0·1020	0·119	−0·170	0·1019	0·178	−0·357
,, ...	0·05000	0·1520	0·177	−0·142	0·1517	0·274	−0·349
$Mg(NO_3)_2$	0·03333	0·1021	0·094	−0·079	0·1020	0·161	−0·326
,,	0·05000	0·1521	0·137	−0·045	0·1519	0·239	−0·306

The consistency of the results obtained by such an indirect method of calculation, which throws all errors on the small concentration of $MgIO_3^{\cdot}$ ion being determined, says much for the accuracy of the solubility measurements. It will be seen that more satisfactory agreement between the magnesium chloride and the nitrate results is obtained by giving B a value of at least 0·34, so that it is probable that B has a value close to this in the two magnesium salt solutions. Taking this value, we may obtain the true dissociation constant of the $MgIO_3^{\cdot}$ ion, $K = k'f_{Mg}f_{IO_3}/f_{MgIO_3}$; if, in the absence of direct evidence, the A factor of equation (2) is given the Debye–Hückel value 0·5, we may write

$$\log K = \log k' - 2\sqrt{\mu} + B\mu,$$

and substituting in this equation the values of k' given in the last column of Table II, we obtain : for the magnesium chloride measurements, $K = 0{\cdot}190$, $B = 2{\cdot}68$; and for the magnesium nitrate results, $K = 0{\cdot}192$, $B = 2{\cdot}42$. The mean values for the $MgIO_3^{\cdot}$ ion are therefore $K = 0{\cdot}19$ and $B = 2{\cdot}6$. These values are of the magnitudes to be expected by analogy with other uni-bivalent salts (Righellato and Davies, *loc. cit.*). The K value may carry a large percentage error, but it is of importance to know even its order of magnitude, since this enables the amount of $MgIO_3^{\cdot}$ ion present in any dilute salt mixture to be computed with an accuracy sufficient for most purposes.

Solubilities in the Presence of Magnesium Sulphate.—There remain for consideration the measurements of LaMer and Goldman using magnesium and zinc sulphates as solvent salts. The single solubility measurement in zinc sulphate is at too high a concentration to be of use, but the other series can be used to study the dissociation of magnesium sulphate. In a bi-bivalent salt solution such as this, thallous iodate will have a lower activity coefficient than in the solutions so far considered, but it can be seen from Fig. 1 that the common equation (4) can safely be assumed to hold good up to an ionic strength of at least 0·02. Only one measurement, for $0{\cdot}005M$-magnesium sulphate, comes within this limit, and calculations have therefore been made for this. They are not given in detail, as they are similar to those just described. The solution contains the following species : $Mg^{\cdot\cdot}$, SO_4'', $Tl^{\cdot}$, IO'_3, $TlIO_3$, $MgIO_3^{\cdot}$, $TlSO'_4$, and $MgSO_4$, and the calculation is directed at finding the ionic strength and hence the concentration of undissociated magnesium sulphate that must be present in order that equation (4) may be satisfied. The calculated concentrations, in millimols. per litre, of the various species in the order named are : 3·681, 3·615, 1·973, 2·039, 0·005, 0·024, 0·090, and 1·295. That is, for equation (4) to be satisfied the magnesium sulphate must be about 25% undissociated. This confirms the conclusion, previously reached, that magnesium sulphate should be regarded as a fairly " weak " electrolyte, and agrees as well as may be expected with the figure deduced from the conductivity and freezing-point data for pure magnesium sulphate, *viz.*, 80% dissociation in $0{\cdot}005M$-solution (Davies, *loc. cit.*).

Summary.

When allowance is made for the incomplete dissociation of the salts concerned, the activity coefficients found for thallous iodate from solubility measurements at 25° lose their abnormal features. The activity coefficient becomes independent of the nature of the added salt provided the concentration of this be small, specific effects not making their appearance with uni-univalent salts until an ionic strength of 0·1 is reached.

The activity coefficient of thallous iodate in the most dilute solutions is expressed by the equation $-\log f = A\sqrt{\mu}$, where $A = 0{\cdot}47$; and, since this A value is much greater than those derived from the most accurate data for other uni-univalent electrolytes, it is concluded that A may vary from salt to salt; it appears to be always lower than the Debye–Hückel value 0·50.

It is shown that the solubility data for thallous chloride and iodate contribute no support, as stated by LaMer and Goldman, for the principle of specific interaction.

The dissociation constant of the $MgIO_3^{\cdot}$ ion is calculated to have the approximate value $K = 0{\cdot}19$.

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