

CCCXVI.—*The Calculation of Activity Coefficients from Solubility Measurements. Part III. The Unsymmetrical Valence Type Effect.*

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WHEN the activity coefficient of a sparingly soluble salt is estimated from its solubility in other salt solutions, there have usually been found small but definite deviations from the principle that the ionic strength of the solution alone governs the activity coefficient; in Parts I and II of this series (this vol., p. 949; preceding paper) it has been shown that these specific deviations are due wholly to use of the incorrect assumption that the salts concerned are completely dissociated into ions. There have also, however, been noticed (Brønsted and Petersen, *J. Amer. Chem. Soc.*, 1921, **43**,

2265; Brönsted and LaMer, *ibid.*, 1924, **46**, 555) certain mixtures where the deviations are altogether greater; so great, in fact, as to call in question the principle of ionic strength, and the Debye-Hückel treatment of dilute electrolyte solutions. A measurement by LaMer and Cook (*J. Amer. Chem. Soc.*, 1929, **51**, 2622) on the solubility of luteocobaltic diamminotetranitrocobaltiate may be cited as an example. When pure water is replaced by 0.0002M-potassium sulphate, the solubility increase should, on the Debye-Hückel theory, be 5.5×10^{-6} mol. per litre. It is actually 14.6×10^{-6} , so that even in such an excessively dilute solution as this, the solubility increase is almost 200% too great, and the limiting laws appear completely at fault. This anomaly has been called the "electric type effect" or the "unsymmetric valence type effect," and has been the subject of a special investigation by LaMer and Mason (*J. Amer. Chem. Soc.*, 1927, **49**, 410) and LaMer and Cook (*loc. cit.*). The anomaly is most marked when the electrolyte mixture contains two ions of high valency and opposite charge, and this suggests that corrections for the incomplete dissociation of the salts concerned may remove these large deviations, just as they have the smaller deviations already investigated; for the dissociation constants so far obtained (Davies, *Trans. Faraday Soc.*, 1927, **23**, 351; Righellato and Davies, *ibid.*, 1930, **26**, 592) lead to the rule that the dissociation constant of a salt or complex ion is determined mainly by the electrical charges of the component ions, being smaller the greater the opposite charges, and only to a minor extent by their specific characteristics; so that the correction for incomplete dissociation will be large in just those cases where the anomaly is greatest.

The object of the present paper is to test this idea quantitatively on some of the data obtained by LaMer and his co-workers. In the two papers cited, they have measured the solubilities of luteocobaltic diamminotetranitrocobaltiate (LN_3) and luteocobaltic diamminodinitro-oxalatocobaltiate (LO_3) in very dilute potassium sulphate solutions, and LaMer and Goldman (*J. Amer. Chem. Soc.*, 1929, **51**, 2632) have published similar data for lanthanum iodate as solute. These measurements are of high accuracy and are particularly suited to our purpose; the solubility relationships of the salt LN_3 will first be considered.

Solubilities of the Salt LN_3 in Potassium Sulphate Solutions.—When the ter-univalent salt LN_3 is dissolved in potassium sulphate solutions, a large number of species are possibly present in the solution, e.g., K^+ , SO_4^{--} , KSO_4^+ , K_2SO_4 , KN , LSO_4^+ , $L(SO_4)_2^+$, L^{+++} , N' , LN'' , LN_2^+ , and LN_3 . If we restrict ourselves to very dilute solutions, however, only first-stage association products will be present

in appreciable amounts, and allowance need not be made for such species as K_2SO_4 , LN_2^* and so on. Further, at concentrations of potassium sulphate not greater than $0.001M$, this salt can be treated as completely dissociated (Righellato and Davies, *loc. cit.*), and the same is undoubtedly true of the uni-univalent salt KN . Finally, the solubility of the salt LN_3 in water is only 1.6×10^{-4} mol. per litre, and no great error can be involved in neglecting the extremely small, almost constant, proportion of LN'' which may be present in the solution. At these high dilutions, therefore, we need only consider the possibility of association between the two ions of high valency, L''' and SO_4'' , and the salts can otherwise be taken as completely dissociated. If, now, we assume that the Debye-Hückel limiting equation $-\log f_{\pm} = 0.5 z_1 z_2 \sqrt{\mu}$ (where f_{\pm} is the mean activity coefficient of a salt, z_1 and z_2 are the valencies of its constituent ions, and μ is the ionic strength) is obeyed by the solutions, and ascribe the deviation of the actual from the theoretical solubility to the formation of the ion LSO_4^* , the amount of this in each solution can be calculated. The test of the theory will lie in whether the results at the various concentrations conform to the requirements of the law of mass action.

The method of calculation is as follows. The solubility of LN_3 in water at 25° is 1.641×10^{-4} mol. per litre. If the salt is completely dissociated, the ionic strength is six times the solubility, and from the Debye-Hückel equation $-\log f_{\pm} = 1.5\sqrt{\mu}$. It follows that the solubility product is $f_{\pm}^4 \cdot m_1 m_2^3 = 1.27 \times 10^{-14}$. Now in potassium sulphate solution of concentration m , let the new solubility be s , and the concentration of LSO_4^* ion be x . The ionic strength is given by $\mu = 3m + 6s - 6x$, and the solubility-product principle yields the equation

$$f_{\pm}^4 (s - x)(3s)^3 = 1.27 \times 10^{-14},$$

or

$$\log (s - x) + 3 \log (3s) - 6\sqrt{\mu} = -13.8962.$$

The two equations can best be solved for x by a series of approximations. The results are in Table I.

TABLE I.

$m \cdot 10^4$.	$s \cdot 10^4$.	$x \cdot 10^4$.	μ .	$\sqrt{\mu}$.	$-\log k'$.	$-\log K$.
0	1.641	—	0.0009846	0.03138	—	—
2	1.787	0.398	0.001432	0.03784	3.253	3.480
5	1.991	0.854	0.002182	0.04671	3.258	3.537
10	2.238	1.28	0.003575	0.05979	3.185	3.544

The first column shows the molar concentration of potassium sulphate, the second the solubility of LN_3 , the third the concentration of LSO_4^* ion, the fourth the ionic strength, the fifth the

square root of this quantity, and the sixth gives the negative logarithm of the "classical" dissociation constant, $k' = m_L m_{SO_4} / m_{LSO_4}$, which should govern the equilibrium $LSO_4 \rightleftharpoons L^{++} + SO_4^{--}$. The last column gives the negative logarithm of the true dissociation constant,

$$K = \frac{f_L f_{SO_4}}{f_{LSO_4}} \cdot \frac{m_L m_{SO_4}}{m_{LSO_4}},$$

which is found from k' by applying the Debye-Hückel equation to give $\log K = \log k' - 6\sqrt{\mu}$. It will be seen that over a fairly considerable concentration range the constancy of K is satisfactory.

Solubilities of the Salt LO_3 in Potassium Sulphate Solutions.—Similar calculations may be applied to the data for the salt LO_3 , and the results provide a decisive test of the theory; for the deviations of this salt from ideal behaviour must be ascribed to the formation of the same ion, the LSO_4 ion, as in the former case, and we should therefore find the same dissociation constant. The results of the calculations are shown in Table II, where the column headings have the same significance as in Table I.

TABLE II.

$m \cdot 10^4$.	$s \cdot 10^4$.	$x \cdot 10^4$.	μ .	$\sqrt{\mu}$.	$-\log k'$.	$-\log K$.
0	0.8255	—	0.0004953	0.02226	—	—
2	0.9236	0.252	0.001003	0.03167	3.332	3.522
5	1.0360	0.481	0.001833	0.04281	3.283	3.539
10	1.1701	0.699	0.003282	0.05729	3.203	3.547

The value of K is again satisfactorily constant, and moreover is in very close agreement with the value derived from the other series of measurements already discussed. The explanation offered of the "unsymmetric valence type effect" seems, therefore, to be fully upheld.

With reference to Table II, it should be mentioned that in LaMer and Cook's paper the solubility of LO_3 in 0.0002M-potassium sulphate is given as 0.90236×10^{-4} . This value was first used in the calculations, but failed to give good agreement with the other two measurements; closer examination then showed that a misprint had arisen, the correct solubility being 0.9236×10^{-4} .

The values of $\log K$ given in Tables I and II, while satisfactorily constant, show a definite and (except the first value of Table I) quite regular trend with changing concentration. This is attributed to a slight error in the one important assumption made in the calculation, *viz.*, that the Debye-Hückel limiting equation holds good; doubt has already been thrown on the correctness of the numerical constant, 0.50, in this equation, and somewhat smaller values have been empirically derived (see, *e.g.*, Parts I and II).

Calculations show that if a value 0.48 is used throughout in place of the value 0.50, the variation in K entirely disappears, the values being as follows: in Table I, $-\log K = 3.522, 3.558, 3.557$; in Table II, $-\log K = 3.547, 3.555, 3.557$.

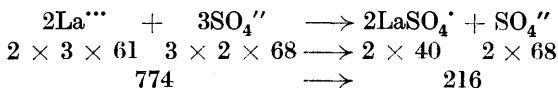
Solubilities of Lanthanum Iodate in Potassium Sulphate Solutions.—The measurements of LaMer and Goldman, using lanthanum iodate as saturating salt, are open to the same treatment. The results of the calculations are given in Table III, where x now represents the concentration, and K the dissociation constant, of the LaSO_4^+ ion.

TABLE III.

$m \cdot 10^4$.	$s \cdot 10^4$.	$x \cdot 10^4$.	μ .	$\sqrt{\mu}$.	$-\log k'$.	$-\log K$.
0	8.9006	—	0.005340	0.07308	—	—
2	9.1666	0.806	0.005616	0.07494	2.907	3.357
5	9.7463	2.731	0.005709	0.07556	3.235	3.688
10	10.564	4.619	0.006567	0.08104	3.159	3.646
20	12.153	7.499	0.008792	0.09377	3.110	3.673

The theoretical value, 0.50, of the numerical constant in the Debye-Hückel equation has been used in this case. The uniformity of the K values is not quite so good, but there is no evidence of a definite trend over the ten-fold change in concentration.

The Dissociation of the LaSO_4^+ Ion from Conductivities.—There are no other suitable solubility measurements, but the dissociation constant just derived can be roughly checked by conductivity measurements. The conductivity of lanthanum sulphate at 18° has been measured by Noyes and Johnston (*J. Amer. Chem. Soc.*, 1909, **31**, 987), who found $\Lambda_0 = 129$ for the equivalent conductivity at infinite dilution, and $\Lambda = 60.1$ for that of a $0.002N$ -solution. Now if lanthanum sulphate were completely dissociated, its conductivity would be given by the equation of Onsager (*Trans. Faraday Soc.*, 1927, **23**, 341), $\Lambda = \Lambda_0 - a\sqrt{C}$, where C is the equivalent concentration and the constant a has in this case the value 469. For a $0.002N$ -solution this gives a conductivity decrease of only 20 units, and the difference between the theoretical value for the conductivity, 109, and the experimental value, 60.1, must be ascribed to partial association of the ions. As we have seen, the first stage in this association will be the formation of the LaSO_4^+ ion, and this stage will probably go almost to completion before the further association of this univalent ion need be considered. The attendant decrease in conductivity may be estimated from the scheme



where 61 and 68 are the mobilities at infinite dilution of the lanthanum and sulphate ions, and 40 may be taken as a rough estimate of the mobility of the LaSO_4^+ ion. The fall in conductivity for 100% association (reckoned on mobilities at infinite dilution) is therefore 558 units per mol., or 93 units per equiv.; *i.e.*, 72%. The observed fall in conductivity is 49 units, or 45%. The degree of association is therefore $45/0.72 = 62\%$. This gives for the individual molar concentrations: La^{3+} , 0.000253; SO_4^{2-} , 0.000587; LaSO_4^+ , 0.000413; and hence, $-\log k' = 3.444$, $\mu = 0.00252$, and $-\log K = 3.745$. This agrees, within the limit of accuracy of the calculations, with the former value. The large deviations from the Debye-Hückel activity theory ("the unsymmetric valence type effect") and the equally large deviations from the Onsager conductivity equation find, therefore, a common explanation in the extensive association between oppositely charged ions of high valency.

Summary.

The large deviations from the Debye-Hückel theory of dilute solutions which have been described as "the electric type effect" or "the unsymmetric valence type effect" are considered to be due wholly to the incomplete dissociation of the salts concerned. Calculations based on solubility measurements with two luteocobaltic salts in potassium sulphate solutions support this view, and give closely concordant values for the dissociation constant of the luteocobaltic sulphate kation. The large deviations found with lanthanum iodate in sulphate solutions are successfully interpreted in the same way, and lead to a value for the dissociation constant of the lanthanum sulphate kation agreeing with that derived from the conductivity of lanthanum sulphate solutions.