55. *The Conductivity of Calcium Iodate and its Solubility in Salt Solutions.*

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The conductivity of calcium iodate in water has been measured at 18°. The results show that the salt, like other iodates, can be regarded as incompletely dissociated, and a value $K = 0{\cdot}13$ is derived for the dissociation constant of the intermediate ion $CaIO_3$. Determinations have also been made of the solubility of the salt in water and numerous salt solutions at 25°. The solubility is very markedly dependent on the nature of the added salt, but corrections for incomplete dissociation remove the anomalies and give values for the mean ionic activity coefficient which lie approximately on a common curve. The measurements in sodium mandelate solutions confirm the dissociation constant of calcium mandelate reported in the preceding paper.

IN pursuance of previous work (see J., 1935, 1416) the solubility of calcium iodate hexahydrate has been measured in a number of salt solutions at 25°. In the interpretation of the results, conductivity data for the pure iodate were required, and these were obtained by measurements at 18°.

The salt was prepared by dropwise addition of solutions of potassium iodate and calcium chloride in equivalent amounts to a large volume of conductivity water. The crystalline hexahydrate separated, and was washed first by decantation and then in the solubility tubes until a constant solubility was attained. In the calculations the value 389·9 has been used for the molecular weight of the anhydrous salt. The solubility measurements were at 25° ± 0·01° and were carried out in the same way as the measurements on barium iodate (Macdougall and Davies, J., 1935, 1416), except that weighed samples were taken for analysis, and the densities of the saturated solutions were determined. The conductivity measurements, at 18° ± 0·005° were carried out as described in earlier papers (see J., 1937, 432), readings being taken at two frequencies, 1000 and 3150. The more concentrated solutions were prepared by weight dilution of an almost saturated stock solution the concentration of which was determined by analysis, and the more dilute solutions by addition of stock solution from a weight burette to conductivity water in the cell. For the more concentrated solutions the relative density could not be taken as unity, and was assumed to be the same at 18° as at 25°.

The conductivity results, based on the Jones and Bradshaw standard, are given in Table I; line 1 shows the equivalent concentration, C, and line 2 the equivalent conductivity, after subtraction of the conductivity of the solvent. At the higher concentrations the conductivity is abnormally low, and the method of the preceding paper was used to calculate $(1 - \alpha)$, the fraction of calcium in the form of the intermediate ion, $CaIO_3^{\bullet}$; the results are in line 3. In the calculations the equivalent conductivity of calcium iodate at zero concentration was taken to be 85·24; this is the value given by the sum of Kohlrausch's mobilities (see Davies, "Conductivity of Solutions," 2nd Edn., p. 205), reduced by 0·09% to correct to the Jones and Bradshaw standard (J., 1937, 1326), and it is also consistent with our measurements in the most dilute solutions. For the mobility of the calcium iodate ion the value 34·0 was adopted.

TABLE I.

The conductivity of calcium iodate at 18°.

$C \times 10^4$ ...	2·000	2·633	4·279	5·876	8·852	11·693	38·77	52·94	58·15	81·85
Λ	83·20	82·83	82·42	81·67	80·88	80·28	76·44	74·95	74·43	72·73
$100\,(1 - \alpha)$	—	—	—	—	—	—	$1{\cdot}9_5$	$2{\cdot}7_7$	$3{\cdot}1_3$	$3{\cdot}9_0$
$10^4 . I$	—	—	—	—	—	—	57·40	77·93	85·40	119·6
$10^2 . \sqrt{I}$ ...	—	—	—	—	—	—	7·580	8·828	9·241	10·94
K	—	—	—	—	—	—	0·140	0·126	0·121	0·126

Lines 4 and 5 of the table give the ionic strength and its square root, and line 6 the dissociation constant of the calcium iodate ion, calculated from the relation:

$$\log K = \log \alpha\,(1 + \alpha)m/(1 - \alpha) - 2{\cdot}02\,\sqrt{I} + 2I$$

The results are satisfactorily constant, and the value $K = 0{\cdot}13$ is adopted.

The results of the solubility measurements are illustrated in the figure and given in Table II, in which col. 1 gives the concentration of the solvent salt and col. 3 the solubility of calcium iodate, both in millimols./l., and col. 2 gives the density of the solution. Where a comparison is possible, the results are generally in good agreement with the determinations of Kilde (*Z. anorg. Chem.*, 1934, **218**, 113), the two values for the salt in water being identical; but for the solubilities in calcium chloride Kilde's results, whilst agreeing with ours in the most dilute solution and also at 0·05M-calcium chloride, are higher at 0·025M.; both values at this concentration are shown in the table. We have not checked our value,

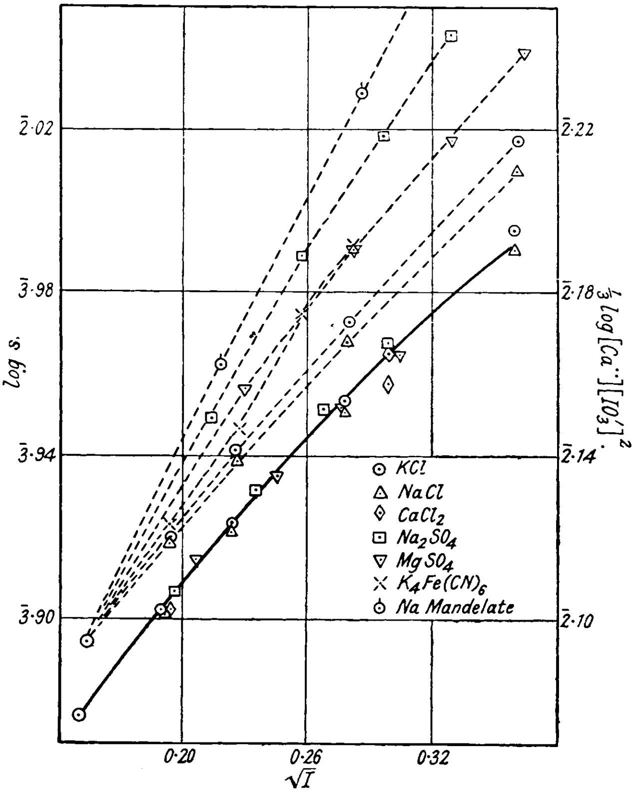
TABLE II.

m.	$d^{25^\circ}_{4^\circ}$.	*s.*	[$CaIO_3^{\cdot}$].				*I.*	$\frac{1}{3}\log[Ca^{\cdot\cdot}][IO_3']^2$	$f_{\pm}$.	Δ.
Water.										
—	0·9998	7·840	0·479	—	—	—	0·02257	$\bar{2}$·0769	0·742	−0·003
Sodium chloride solutions.										
				[$NaIO_3$].						
12·5	1·0010	8·285	0·472	0·047	—	—	0·03686	$\bar{2}$·1012	0·702	+0·003
25·0	1·0015	8·676	0·476	0·093	—	—	0·04998	$\bar{2}$·1211	0·670	+0·001
50·0	1·0025	9·287	0·482	0·187	—	—	0·07671	$\bar{2}$·1502	0·627	+0·003
100·0	1·0050	10·23	0·507	0·382	—	—	0·1293	$\bar{2}$·1903	0·572	±0·000
Potassium chloride solutions.										
				[KIO_3].						
12·5	1·0008	8·312	0·476	0·070	—	—	0·03642	$\bar{2}$·1022	0·700	±0·000
25·0	1·0017	8·730	0·480	0·140	—	—	0·05009	$\bar{2}$·1231	0·667	−0·001
50·0	1·0032	9·387	0·490	0·282	—	—	0·07690	$\bar{2}$·1533	0·622	−0·002
100·0	1·0057	10·42	0·521	0·577	—	—	0·1296	$\bar{2}$·1955	0·565	−0·007
Calcium chloride solutions.										
6·25	1·0001	6·692	0·591	—	—	—	0·03765	$\bar{2}$·1019	0·701	+0·004
25·0	1·0016	5·444	0·868	—	—	—	0·08959	$\bar{2}$·1576	0·616	+0·007
25·0	—	5·57*	0·88	—	—	—	0·8994	$\bar{2}$·1649	0·606	−0·002
50·0	1·0036	4·900	1·177	—	—	—	0·1623	$\bar{2}$·2005	0·558	+0·007
Sodium sulphate solutions.										
				[$NaIO_3$].	[$CaSO_4$].	[$NaSO_4'$].				
6·25	1·001	8·898	0·451	0·049	1·445	0·132	0·03845	$\bar{2}$·1071	0·692	−0·002
12·5	1·002	9·745	0·440	0·102	2·397	0·475	0·05523	$\bar{2}$·1315	0·655	−0·003
18·75	1·003	10·45	0·436	0·157	3·121	0·970	0·07215	$\bar{2}$·1512	0·626	−0·005
25·0	1·004	11·05	0·428	0·213	3·724	1·586	0·08916	$\bar{2}$·1673	0·603	−0·006
Magnesium sulphate solutions.										
				[$MgIO_3^{\cdot}$].	[$CaSO_4$].	[$MgSO_4$].				
6·25	1·001	9·038	0·459	0·253	1·281	0·772	0·04248	$\bar{2}$·1141	0·681	−0·003
12·5	1·002	9·788	0·446	0·481	2·044	2·292	0·06017	$\bar{2}$·1349	0·649	±0·000
18·75	1·004	10·42	0·443	0·707	2·623	4·167	0·07680	$\bar{2}$·1517	0·625	+0·001
25·0	1·004	10·95	0·441	0·936	3·104	6·275	0·09256	$\bar{2}$·1647	0·606	+0·001
Potassium ferrocyanide solutions.										
1·25	1·0007	8·377	—	—	—	—	—	—	—	—
2·5	1·0013	8·839	—	—	—	—	—	—	—	—
3·75	1·0018	9·430	—	—	—	—	—	—	—	—
5·0	1·0023	9·804	—	—	—	—	—	—	—	—
Sodium mandelate solutions.										
				[$NaIO_3$].	[$CaM^{\cdot}$].				*K.*	
20·0	1·0002	9·177	0·440	0·081	1·902	—	0·04277	$\bar{2}$·1124	0·033	
50·0	1·0047	10·69	0·420	0·218	3·765	—	0·07348	$\bar{2}$·1490	0·036	
100·0	1·0090	12·83	0·396	0·486	6·506	—	0·1242	$\bar{2}$·1870	0·036	

* Kilde's determination (*loc. cit.*).

as our collaboration ended before Kilde's paper appeared, but we think that probably it is low; a possible explanation is that the time required to effect saturation is much longer in solutions containing a common ion, and that for this measurement saturation had not been attained.

If now we assume all the salts concerned to be completely dissociated and apply the conventional treatment to our results, we have (except for the calcium chloride series where the presence of the common ion modifies the formula) $4\gamma^3s^3 = S_0$, where γ is the mean (stoicheiometric) activity coefficient, s the solubility, and S_0 the solubility product. The relation can be written as $\log s = \text{const.} - \log \gamma$, and a graph of $\log s$ against the square root of the ionic strength will show whether the changes in $\log \gamma$ are consistent with the Debye–Hückel activity theory. The curves shown by broken lines in the figure illustrate this treatment. The solubilities depend to a far greater extent than would have been expected on the nature of the added salt, the deviations of one from another being most marked even at the lowest concentrations. So far as the results in sodium and magnesium sulphates are concerned, the anomalies fall into line with those observed by Brönsted and LaMer many years ago (cf. Brönsted and Petersen, *J. Amer. Chem. Soc.*, 1921, **43**, 2265; LaMer and Cook, *ibid.*, 1929, **51**, 2622) and characterised by them as "The Electric Type Effect," or "The Unsymmetrical Valence Type Effect." But the striking feature of the present measurements is that the greatest anomaly is found with the uni-univalent salt sodium mandelate, which actually affects the solubility of calcium iodate more than twice as much as sodium or potassium chloride of the same concentration. It will be shown below that this anomaly is quantitatively explained by corrections for ion-association, just as the " Unsymmetrical Valence Type Effect " was accounted for in an earlier paper (J.,.1930, 2421).



To make allowance for ion association, the compositions of the solutions must be calculated in terms of the actual concentrations of the ions and non-conducting molecules present in each. This has been done for the measurements in the chloride and sulphate solutions by using equations of the form $\log [XY] = \log [X][Y] - \log K - A\sqrt{I} + BI$, where [XY] is the concentration of a non-conducting molecule or intermediate ion, and the values of the constants K, A, and B, taken from this or earlier papers, are :

	$CaIO_3{}^{\cdot}$.	$NaIO_3$.	KIO_3.	$MgIO_3{}^{\cdot}$.	$CaSO_4$.	$MgSO_4$.	$NaSO_4{}'$.
K	0·13	3·0	2·0	0·19	0·0053	0·0063	0·20
A	2·02	1·01	1·01	2·02	4·04	4·04	2·02
B	2·0	1·0	1·0	2·6	4·0	4·0	1·3

The chlorides were assumed to be completely dissociated. Similar calculations for the potassium ferrocyanide series are precluded by lack of data. Approximate calculations (*J. Amer. Chem. Soc.*, 1937, **59**, 1760) make it probable that the solutions investigated contain considerable amounts of the ions $KFe(CN)_6{}'''$ and $K_2Fe(CN)_6{}''$, and the presence in varying amounts of these, together with the products of their association with calcium ions, may account for the unusual shape of the uncorrected curve.

The results of the calculations are given in cols. 4—7 of Table II, which show the concentrations in millimols. of the products of association ; the concentrations of the other ionic species can be found by subtraction, and hence the ionic strength shown in col. 8. We can now apply the solubility product principle in its accurate form, $f_{\pm}{}^3[Ca^{\cdot\cdot}][IO'_3]^2 = S_0$, where $f_{\pm}$ is the mean ionic activity coefficient, and in place of the expression $\log s = \text{const.} - \log \gamma$ we have $\frac{1}{3} \log [Ca^{\cdot\cdot}][IO'_3]^2 = \text{const.} - \log f_{\pm}$. Values of the term on the left-hand side of this expression are given in col. 9 of the table, and are plotted against the square root of the ionic strength in the lower series of points (right-hand scale of co-ordinates) in the figure.

It will be seen that the corrections remove the large anomalies in every case, and the points all lie close to a common curve. The determination of activity coefficients from these results involves an extrapolation of the curve to zero ionic strength, and this, on account of the relatively high solubility of calcium iodate, is somewhat uncertain. Use can here be made of the earlier results with barium iodate (Macdougall and Davies, *loc. cit.*). These, as would be expected on theoretical grounds, can by a transposition of scale be accurately superimposed on the corrected calcium iodate results; and as they extend down to an ionic strength of 0·0025, at which the limiting Debye–Hückel equation is valid, the extrapolation presents no difficulty. The extrapolated value for the solubility product is $6{\cdot}953 \times 10^{-7}$, and from this the mean ionic activity coefficients shown in col. 10 of the table are obtained. Col. 11 shows the deviation $\Delta = f_{\pm\text{expt.}} - f_{\pm\text{eqn.}}$, where the latter values are obtained from the empirical equation $-\log f_{\pm} = 1{\cdot}01\sqrt{I}/(1 + \sqrt{I}) - 0{\cdot}19I$. This form of equation, suggested by Dr. E. A. Guggenheim, is valid at higher ionic strengths than the Brönsted equation, $-\log f_{\pm} = 1{\cdot}01\sqrt{I} - BI$, used in previous papers from this laboratory. The agreement is good, and below an ionic strength of 0·1, at any rate, there is no consistent increase in the deviation with increasing ionic strength; this suggests that the deviations are no greater than the errors of experiment and calculation.

For the measurements in sodium mandelate solutions this equation was used to calculate values of $\frac{1}{3}\log[\text{Ca}^{\cdot\cdot}][\text{IO}_3{}']^2$, and hence the amount of calcium mandelate necessarily present was obtained by successive approximations; allowance for the calcium iodate cation was made as before, whilst sodium mandelate is known to be completely dissociated (Banks and Davies, this vol., p. 73). The results are in the table, where the last column now shows the dissociation constant of calcium mandelate calculated from the equation $\log K = \log[\text{Ca}^{\cdot\cdot}][\text{M}']/[\text{CaM}^{\cdot}] - 2{\cdot}02\sqrt{I} + 2{\cdot}7I$ (cf. preceding paper). The values are satisfactorily constant, and agree with the figure $K = 0{\cdot}035$ obtained in the preceding paper by an entirely different method.

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