251. *The Equilibrium* $Fe^{\cdot\cdot\cdot} + I' \rightleftarrows Fe^{\cdot\cdot} + \frac{1}{2}I_2$ *in Aqueous Solution.*

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IN accordance with the important part which is played by inter-ionic forces in dilute solutions of electrolytes, it has been found that the mass action coefficient for the equilibrium $Fe^{\cdot\cdot\cdot} + I' \rightleftarrows Fe^{\cdot\cdot} + \frac{1}{2}I_2$ given by

$$K_1 = [Fe^{\cdot\cdot}][I_2]^{\frac{1}{2}}/[Fe^{\cdot\cdot\cdot}][I'] \quad . \quad . \quad . \quad . \quad (1)$$

varies very considerably when the relative proportions or the absolute concentrations of the reactants are changed. If, however, the equilibrium is established in an aqueous solution in which the ionic environment is stabilised by the presence of a relatively large quantity of a foreign electrolyte, it would seem that the equilibrium relations should conform to the requirements of the classical mass action law and that K_1 should be constant.

Brönsted and Pedersen (*Z. physikal. Chem.*, 1923, **103**, 307) have recently studied this equilibrium in a solution containing 1·65 mols. of potassium chloride per litre (with the addition of 0·1 mol. of hydrogen chloride to prevent hydrolysis of the ferric salt), and claim to have shown that the mass law holds under these conditions and that the value of K_1 at 25° is 21·1. These authors have taken account of the fact that the concentration of the free iodine is affected by the formation of tri-iodide (I_3'), but have omitted to realise that the formation of di-iodochloride (ClI_2') has a similar influence on the proportion of the titratable iodine which is actually in the free condition. For this reason, the proof of the validity of the mass law and the value assigned to K_1 are unacceptable and the present authors have undertaken a further study of the equilibrium. In addition to variations in the relative and absolute concentrations of the reactants in an ionic solvent of fixed composition, the experiments to be described include an investigation of the effect of changes in the concentration of the relatively concentrated potassium chloride solutions which are used to stabilise the ionic environment.

The following is a brief outline of the method which has been used for the determination of K_1. It is assumed that the equilibrium in question has been established by dissolving weighed quantities of anhydrous ferric chloride and potassium iodide in the acidified concentrated solution of potassium chloride, and that the resulting solution has been titrated with standard thiosulphate.

As a consequence of complex formation the constitution of the final solution is dependent on the equilibria represented by

$$ClI_2' \rightleftharpoons Cl' + I_2 \text{ corresponding with } K_2 = [Cl'][I_2]/[ClI_2'] \quad (2)$$

and $$I_3' \rightleftharpoons I' + I_2 \text{ corresponding with } K_3 = [I'][I_2]/[I_3'] \quad . \quad (3)$$

If now a denotes the total original iodide concentration (equivs. per litre of potassium iodide used in the preparation of the solution), b the total chloride concentration (equivalents per litre of $KCl + HCl + FeCl_3$), and c the total iodine (mols. per litre as determined by thiosulphate titration of the final solution) we have

$$[I'] + 2[I_2] + 3[I_3'] + 2[ClI_2'] = a \quad . \quad . \quad . \quad (4)$$

$$[Cl'] + [ClI_2'] = b \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$[I_2] + [I_3'] + [ClI_2'] = c \quad . \quad . \quad . \quad . \quad (6)$$

The concentration of free iodine $[I_2]$ being represented by d, equations (2)—(6) may be shown to lead to the relations

$$[ClI_2'] = bd/(K_2 + d) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$[I_3'] = c - d - bd/(K_2 + d) \quad . \quad . \quad . \quad . \quad (8)$$

$$[I'] = a - 3c + d + bd/(K_2 + d) \quad . \quad . \quad . \quad (9)$$

in which the concentrations of the simple and complex iodine-containing ions are expressed in terms of the known quantities a, b, and c, the constant K_2, and the concentration of free iodine d. If d, which is of the order of magnitude of 0·0001, is neglected in comparison with $K_2 = 0{\cdot}6$, it may be shown further that d is given by

$$d = \sqrt{K_2K_3c/(b + K_2) + e^2} - e \quad . \quad . \quad . \quad (10)$$

where $e = \{K_2(a - 3c) + K_3(b + K_2)\}/2(b + K_2)$

It follows that the concentrations of all the substances which are directly involved in the equilibrium $Fe^{\cdot\cdot\cdot} + I \rightleftharpoons Fe^{\cdot\cdot} + \frac{1}{2}I_2$ can be derived from the composition of the original solution and the thiosulphate titration of the equilibrium solution provided that the constants K_2 and K_3 are known for the concentrated potassium chloride solutions which are used as the solvent in the study of the relations expressed by equation (1).

Determination of K_2 *for the Equilibrium* $ClI_2' \rightleftharpoons Cl' + I_2$.—The value of K_2 has been derived from the measurement of the solubility of iodine in solutions of potassium chloride. The titratable iodine content of these solutions depends, not only on the extent to which the complex ion ClI_2' is formed, but also on the salting-out effect of the chloride. If b is the total chloride concentration, c the titratable iodine concentration, and d the free iodine concentration, we may write

$$[ClI_2'] = c - d,\ [Cl'] = b - c + d,\ d = d_0e^{-\gamma b}$$

and

$$K_2 = (b - c + d)d/(c - d)$$

where $d_0 = 0{\cdot}00132$ is the value of d when pure water is the solvent and γ is the coefficient which expresses the salting-out effect of the chloride in the solvent medium. The value of γ has been obtained by the method described by Dawson and Carter (*Proc. Leeds Phil. Soc.*, 1925, **1**, 14), which leads to $\gamma = 0{\cdot}172$.

Table I summarises the results obtained with (A) neutral KCl solutions, (B) KCl solutions containing 0·1 mol. of HCl per litre. In the latter series the salting-out effect of the hydrochloric acid is very small in comparison with that of the potassium chloride and has been neglected in the calculation of the free iodine concentration (d).

TABLE I.

A	b	0·5	0·7	1·0	1·5	1·65	2·0	2·5	3·0
	$10^3\,c$	2·172	2·460	2·855	3·440	3·575	3·875	4·245	4·495
	$10^3\,d$	1·211	1·170	1·110	1·020	0·994	0·936	0·859	0·788
	K_2	0·629	0·635	0·636	0·633	0·635	0·636	0·633	0·637
B	b	0·6	1·10	1·75	2·1	3·1			
	$10^3\,c$	2·377	3·030	3·695	3·955	4·530			
	$10^3\,d$	1·211	1·110	0·994	0·936	0·788			
	K_2	0·622	0·635	0·643	0·650	0·652			

The values of K_2 in series A remain remarkably constant whilst the chloride concentration is raised from 0·5 to 3·0 mols. per litre; those in series B show a tendency to increase slightly. Since the relation between K_2 and the corresponding thermodynamic constant is given by $K_2{}^a = K_2 f_{Cl'} f_{I_2}/f_{ClI_2'}$, it may be inferred that the activity coefficient ratio $f_{Cl'}/f_{ClI_2'}$ is independent of the chloride concentration. For the purpose of this paper the value of K_2 will be taken as 0·635.

Determination of K_3 *for the Equilibrium* $I_3' \rightleftharpoons I' + I_2$.—In the absence of other salts, the value of K_3 for dilute iodide solutions at 25° is 0·00138 (Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19). It cannot, however, be assumed that this value will hold for concentrated solutions of potassium chloride, and the influence of the latter has been determined by measuring the solubility of iodine in such solutions containing variable and relatively small quantities of potassium iodide. Having regard to the circumstance that the K_3 values are to be utilised in the determination of K_1, the chloride solutions were in every case acidified by the addition of 0·1 mol. of hydrochloric acid per litre. Since the iodide concentrations are very small, the salting-out effect is determined by the chloride content of the solutions, and it follows that the concentration of the free iodine, as well as that of the complex ClI_2', will be practically the same as in the corresponding chloride solutions which are free from iodide (compare Table I, Series *B*). Under these conditions, the required values of I′ and I_3' are given by the relations $[I'] + [I_3'] = a$, and $[I_2] + [I_3'] + [ClI_2'] = c$.

The results obtained for the series of solutions with 1·65KCl + 0·1HCl + *a*KI as solvent are shown in Table II, in which *c* represents the measured solubility of iodine in mols. per litre at 25°.

TABLE II.

$I_2 = 0{\cdot}000994$; $ClI_2' = 0{\cdot}00270$.

a	0	0·005	0·01	0·015	0·02	0·025	0·04	0·056	0·08
$10^3\, c$	3·695	5·52	7·45	9·38	11·32	13·27	19·12	25·50	35·35
$10^3\, I_3'$	—	1·825	3·755	5·685	7·625	9·575	15·43	21·85	31·67
$10^3\, I'$	—	3·175	6·245	9·315	12·37	15·42	24·55	34·15	48·35
$10^3\, K_3$......	—	1·73	1·65	1·63	1·61	1·60	1·58	1·55	1·52

It is apparent that K_3 is not constant but slowly diminishes as the concentration of the total iodide increases. The results obtained in corresponding series of experiments with solvents in which the concentration of the potassium chloride was 0·5, 1·0, 2·0, and 3·0 mols. show a similar variation of K_3 with the concentration of the iodide, and it seems possible that this may be connected with the formation of small quantities of a higher polyiodide (KI_5).

If the values of K_3 for a fixed concentration of iodide (0·02 mol. per litre) and variable concentrations of chloride are compared, it is found that K_3 increases slowly with the chloride concentration. The actual results are shown in Table III, in which *b* represents the total chloride concentration (KCl + 0·1HCl) and *c* the total iodine concentration of the solution saturated with iodine. In every case the concentrations of the free iodine $[I_2]$ and of the complex di-iodochloride ion $[ClI_2']$ are those which correspond with series *B* in Table I.

TABLE III.

b	0·6	1·10	1·75	2·1	3·1
$10^3\, c$	11·36	11·38	11·32	11·24	10·82
$10^3\, I_3'$	8·98	8·35	7·63	7·28	6·30
$10^3\, I'$	11·02	11·65	12·37	12·72	13·70
$10^3\, K_3$	1·49	1·55	1·61	1·63	1·71

No entirely satisfactory explanation can be offered to account for the variations of K_3 shown in the above tables, but the changes are not of such magnitude as to interfere with the application of the results to the determination of K_1, and for this purpose the values of K_3 recorded in Table III have been taken as a measure of the tri-iodide formation in the several chloride solutions which have been employed as solvents in the investigation of the equilibrium corresponding with K_1. In consequence of the neglect to take account of the formation of ClI_2' ions, the value of $10^3K_3 = 6{\cdot}11$ given by Brönsted and Pedersen is quite erroneous.

Determination of K_1 *for the Equilibrium* $Fe^{\cdots} + I' \rightleftharpoons Fe^{\cdot\cdot} + \frac{1}{2}I_2$.—In the investigation of this equilibrium, the solutions containing weighed quantities of anhydrous ferric chloride and potassium iodide dissolved in the appropriate solvent were kept in a thermostat at 25° until equilibrium was attained (2—3 days). Suitable precautions were taken to avoid contact with air in the preparation of the solutions and in the subsequent manipulation. The samples for analysis were run into an excess of cold water and titrated without delay. The data thus obtained give directly the values of $[Fe^{\cdots}]$ and $[Fe^{\cdot\cdot}]$ and the values of $[I\ ]$ and $[I_2]$ are derived from equations (9) and (10) by the introduction of the values of K_2 and K_3 which are given by the experiments described in the previous sections. Table IV shows the results obtained with 1·65KCl + 0·1HCl as solvent. The first two columns give the molar concentrations of potassium iodide and ferric chloride in the original solutions; the next four give the values of $[Fe^{\cdots}]$, $[Fe^{\cdot\cdot}]$, $[I_2]$, and $[I']$ in the state of equilibrium, and the last records the values of K_1.

TABLE IV.

KI . 10^3.	$FeCl_3$. 10^3.	$[Fe^{\cdots}]$. 10^3.	$[Fe^{\cdot\cdot}]$. 10^3.	$[I_2]$. 10^3.	$[I']$. 10^3.	K_1.
2·50	2·44	1·195	1·245	0·139	1·155	10·6
5·00	4·88	2·125	2·755	0·277	1·915	11·3
12·50	12·20	4·72	7·48	0·615	3·625	10·8
5·00	12·20	8·35	3·85	0·440	0·899	10·8
5·00	24·40	20·02	4·38	0·526	0·466	10·8
12·50	24·40	14·85	9·55	0·948	1·850	10·7
25·00	12·20	1·85	10·35	0·476	11·29	10·8
25·00	24·40	8·69	15·71	1·070	5·57	10·6

The values of K_1 are in close agreement, and $K_1 = 10{\cdot}8$ may be taken as the value of the equilibrium constant in 1·65KCl + 0·1HCl at 25°. For the same solvent, Brönsted and Pedersen obtained $K_1 = 21{\cdot}1$, but if the experimental data of these authors are interpreted in accordance with the procedure described in this paper, their results also give $K_1 = 10{\cdot}8$.

It may consequently be regarded as established that the equilibrium $Fe^{\cdots} + I' \rightleftarrows Fe^{\cdot\cdot} + \frac{1}{2}I_2$ conforms very closely to the classical mass-action law when the ionic environment is stabilised by the use of a concentrated salt solution as the reaction medium. Nevertheless, it may be anticipated on thermodynamic grounds that the value of K_1 will depend on the actual concentration of the salt which is employed to stabilise the ionic atmosphere by eliminating such variations as would result from changes in the concentrations of the reactants directly concerned in the equilibrium.

The relation between K_1 and the corresponding thermodynamic equilibrium constant K_1^a is given by

$$K_1^a = K_1 f_2 f_0^{\frac{1}{2}} / f_3 f_1$$

where f_0, f_1, f_2, and f_3 represent the activity coefficients of the iodine molecule, the iodine ion, the ferrous ion, and the ferric ion respectively.

In accordance with the Debye–Hückel theory, the dependence of the activity coefficients on the ionic strength μ is given, at any rate approximately, by $\log f = -\alpha z^2\sqrt{\mu} + \beta\mu$, where z is the valency of the ion concerned, α a general and β a specific constant. If $\alpha = 0{\cdot}5$, it may be shown that

$$\begin{aligned}\log K_1 &= \log K_1^a - \Sigma\alpha z^2\sqrt{\mu} + \Sigma\beta\mu \\ &= \text{const.} - 3\sqrt{\mu} + (\beta_3 + \beta_1 - \beta_2 - \tfrac{1}{2}\beta_0)\mu\end{aligned}$$

and from what is known of the magnitude of the β values it is extremely probable that the net effect of the μ term will be small in comparison with that of the $\sqrt{\mu}$ term for the available range of μ values. The conclusion may therefore be drawn that the equilibrium constant K_1 will diminish continuously as the ionic strength (determined by the chloride concentration) of the reaction medium increases. That this is actually the case is shown by the results recorded in Table V, which gives the values of K_1 obtained for solutions with potassium chloride concentrations ranging from 0·5 to 3·5 mols. per litre, in each case with the addition of $0{\cdot}1M$-hydrogen chloride. In all these solutions the original concentration of potassium iodide was $0{\cdot}0125M$, and that of the ferric chloride $0{\cdot}0122M$. The value of K_2 throughout is 0·635, and that used for K_3 is shown in the second column.

From the figures in the last column of the table it is apparent that K_1 falls cont nuously as the concentration of the potassium

TABLE V.

KCl, *M*.	$K_3 . 10^3$.	$[Fe^{\cdot\cdot\cdot}] . 10^3$.	$[Fe^{\cdot\cdot}] . 10^3$.	$[I_2] . 10^3$.	$[I'] . 10^3$.	K_1.
0·5	1·49	4·44	7·76	0·985	0·283	19·4
1·0	1·55	4·59	7·61	0·778	0·326	14·2
1·65	1·60	4·72	7·48	0·615	0·362	10·8
2·0	1·63	4·73	7·47	0·561	0·374	10·0
2·5	1·67	4·825	7·375	0·490	0·396	8·55
3·0	1·71	4·85	7·35	0·441	0·409	7·8
3·5	1·73	4·94	7·26	0·395	0·426	6·85

chloride in the reaction medium increases. In a corresponding experiment with 0·1*N*-hydrochloric acid as the solvent (same initial concentrations of KI and $FeCl_3$), the value obtained for K_1 was 41·0. The data for this solvent are not, however, included in the table for the reason that this value of K_1 is not characteristic of the solvent but varies with the concentrations of the reactants directly concerned in the equilibrium.

Summary.

The results described above show that the mass-action coefficient for the equilibrium $Fe^{\cdot\cdot\cdot} + I' \rightleftharpoons Fe^{\cdot\cdot} + \frac{1}{2}I_2$ is constant when provision is made for the maintenance of constant ionic environment by the use of concentrated salt solutions as reaction medium. The analysis of the experimental data for solutions containing potassium chloride involves the appropriate consideration of the simultaneous equilibria $ClI_2' \rightleftharpoons Cl' + I_2$ and $I_3' \rightleftharpoons I' + I_2$. The value of K_1 depends on the salt content of the reaction medium, and decreases from 19·4 to 6·85 when the concentration of potassium chloride in the solvent is increased from 0·5 to 3·5 mols. per litre. This diminution is qualitatively in accordance with theoretical predictions based on a consideration of the relation between the mass action coefficient and the thermodynamic equilibrium constant.

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