

Studies on the Behaviour of Bibivalent Salts in Aqueous Solution: Part II. Zinc Sulphate

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Six types of cells using zinc sulphate alone and zinc sulphate mixed with potassium sulphate, with and without liquid junction potentials, have been studied in order (i) to test whether activity coefficient of single ions can be roughly calculated and used in the study of equilibria, (ii) to see if $\text{Zn}(\text{SO}_4)_2^{2-}$ ions are present in zinc sulphate solutions upto 0.1M and (iii) to measure the value of dissociation constant (K) of zinc sulphate into zinc and sulphate ions. The conclusion regarding (i) is positive and (ii) is negative. Values of K are given by all the cells. The most probable value obtained from $\text{Hg}_y \text{Zn}_x \mid \text{ZnSO}_4 \text{Hg}_2\text{SO}_4 \mid \text{Hg}$, by extrapolating the value to zero concentration is 7.5×10^{-3} .

Dissociation of bibivalent salts has been studied by a number of workers. An account of the work is given by Harned and Owen¹ and Nancollas². Transport measurements with concentrated solutions of zinc sulphate³ suggest complex of $\text{Zn}(\text{SO}_4)_2^{2-}$. The types of cells given below were studied. In the cells Zn_xHg_y is a two phase amalgam of Zn and Hg, containing 5-6% of Zn. The two phases ensure constancy of composition of each phase and hence a constant standard electrode potential.

- (a) $\text{Hg}_y \text{Zn}_x \mid \underset{(c)}{\text{ZnSO}_4} \parallel \text{salt bridge} \parallel \underset{(c)}{\text{Zn}(\text{ClO}_4)_2} \mid \text{Zn}_x\text{Hg}_y$
- (b) $\text{Hg} \mid \text{Hg}_2\text{SO}_4 \underset{(c)}{\text{K}_2\text{SO}_4} \parallel \text{s.b.} \parallel \underset{(c)}{\text{ZnSO}_4} \text{Hg}_2\text{SO}_4 \mid \text{Hg}$
- (c) $\text{Hg}_y \text{Zn}_x \mid \underset{(c)}{\text{ZnSO}_4} \text{Hg}_2\text{SO}_4 \mid \text{Hg}$
- (d) $\text{Hg}_y \text{Zn}_x \mid \underset{(c_1)}{\text{K}_2\text{SO}_4} \underset{(c_2)}{\text{ZnSO}_4} \parallel \text{s.b.} \parallel \underset{(c_2)}{\text{Zn}(\text{ClO}_4)_2} \mid \text{Zn}_x \text{Hg}_y$
- (e) $\text{Hg} \mid \text{Hg}_2\text{SO}_4 \underset{(c_1+c_2)}{\text{K}_2\text{SO}_4} \parallel \text{s.b.} \parallel \underset{(c_1)}{\text{K}_2\text{SO}_4} \underset{(c_2)}{\text{ZnSO}_4} \text{Hg}_2\text{SO}_4 \mid \text{Hg}$
- (f) $\text{Hg}_y \text{Zn}_x \mid \underset{(c_1)}{\text{K}_2\text{SO}_4} \underset{(c_2)}{\text{ZnSO}_4} \text{Hg}_2\text{SO}_4 \mid \text{Hg}$

Cells of the type a, b, d and e are denoted as a_1 , b_1 , d_1 and e_1 respectively when saturated KCl is used as bridge and a_2 , b_2 , d_2 and e_2 when saturated $\text{NH}_4 \text{NO}_3$ is used as bridge.

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1. "Physical Chemistry of Electrolytic Solutions" page 147 (To read 10⁴ K for 100 K).

2. *Quarterly Reviews*, 1960, 14, 402.

3. *J. Amer Chem. Soc.*, 1949, 71, 576.

EXPERIMENTAL

The chemicals used were B.D.H. (Analar) except zinc perchlorate which was prepared as described earlier⁴. Stock solutions of zinc sulphate and zinc perchlorate were prepared and their zinc content was estimated by precipitating as zinc ammonium phosphate and weighing as such. The thermostat, cell vessels and the salt bridges used, the method of preparing and checking the half elements and the process of setting up the cells were as in earlier studies⁵. All the e.m.f. measurements were made in duplicate at $35^\circ \pm 0.1^\circ$ and the duplicates agreed within 0.2 m.v. The measured values of all the cells 'a' to 'f' are given in tables 'I' to 'VI', respectively. Concentrations in all the tables are given in gram moles per liter. The suffix 'T' indicates stoichiometric concentration without taking into account the dissociation or interaction.

TABLE — I — CELL 'a'

$\text{Hg}_y \text{ Zn}_x \mid \text{ZnSO}_4 \text{ (o)} \parallel \text{salt bridge} \parallel \text{Zn(ClO}_4)_2 \text{ (o)} \mid \text{Zn}_x \text{ Hg}_y$						
[Zn (ClO ₄) ₂] _T as well as [ZnSO ₄] _T	E.M.F. (mv)		log ₁₀ a _{Zn²⁺}		K×10 ³	
	a ₁	a ₂	a ₁	a ₂	a ₁	a ₂
0.02	7.5	6.3	3.6845	3.7240	2.26	3.12
0.03	8.2	7.5	3.7799	3.8029	2.00	2.49
0.04	9.6	8.4	3.8276	3.8670	1.78	2.33
0.05	9.8	9.1	3.8895	3.9125	1.83	2.14
0.06	11.1	9.9	3.9041	3.9436	1.49	1.91
0.07	11.1	10.2	3.9524	3.9812	1.46	1.86
0.08	12.0	10.9	3.9675	2.0036	1.39	1.99
0.09	12.4	11.5	3.9933	2.0226	1.36	1.63
0.10	13.0	11.9	2.0083	2.0444	1.29	1.59
Mean					1.6	2.2
Extrapolated to $\sqrt{c}=0$,					2.9	3.6

TABLE — II — CELL 'b'

$\text{Hg} \mid \text{Hg}_2\text{SO}_4 \text{ K}_2\text{SO}_4 \text{ (c)} \parallel \text{salt bridge} \parallel \text{ZnSO}_4 \text{ (o)} \mid \text{Hg}_2\text{SO}_4 \mid \text{Hg}.$						
$[\text{K}_2\text{SO}_4]_{\text{T}}$ as	E.M.F. (mv)		$\log_{10} a_{\text{SO}_4^{2-}}$		$K \times 10^3$	
well as $[\text{ZnSO}_4]_{\text{T}}$	b_1	b_2	b_1	b_2	b_1	b_2
0.02	3.4	4.4	3.7883	3.7554	9.14	5.53
0.03	4.6	5.3	3.8591	3.8361	5.27	4.21
0.04	5.2	6.0	3.9144	3.8884	5.42	3.82
0.05	5.7	6.3	3.9542	3.9349	4.49	3.78
0.06	6.0	6.9	3.9897	3.9601	4.00	3.16
0.07	6.6	7.2	2.0089	3.9892	3.60	3.03
0.08	6.6	7.4	2.0389	2.0127	3.67	2.87
0.09	7.1	7.6	2.0521	2.0494	3.24	3.16
0.10	7.4	8.1	2.0649	2.0419	2.99	2.39
Mean					4.6	3.6
Extrapolated to $\sqrt{c}=0$					8.8	6.4

4. This *Journal*, 1954, **31**, 483.5. This *Journal*, 1951, **28**, 683.

TABLE III — CELL 'c'

$\text{Hg}_y \text{Zn}_x \mid \text{ZnSO}_4 \quad \text{Hg}_2\text{SO}_4 \mid \text{Hg}$				
$[\text{ZnSO}_4]_{\text{T}}$	E.M.F. in volts.	$*E_o$	$**E_o$	$K \times 10^3$
0.02	1.4994	1.3613	1.3615	6.82
0.03	1.4936	1.3606	1.3606	5.59
0.04	1.4898	1.3599	1.3603	4.94
0.05	1.4866	1.3598	1.3599	4.74
0.06	1.4843	1.3591	1.3594	4.39
0.07	1.4822	1.3590	1.3593	4.17
0.08	1.4805	1.3587	1.3590	4.03
0.09	1.4790	1.3584	1.3593	3.89
Mean		1.3596	1.3599	4.82
Extrapolated to $\sqrt{c}=0$		1.3624	1.3624	7.5

$*E_o$ is E_o calculated with a_{Zn}^{2+} from Cell a_1 and $a_{\text{SO}_4}^{2-}$ from cell b_1 i.e. with KCl bridge.

$**E_o$ is E_o calculated with a_{Zn}^{2+} from cell a_2 and $a_{\text{SO}_4}^{2-}$ from cell b_2 i.e. with NH_4NO_3 bridge.

TABLE IV — CELL 'd'

$\text{Hg}_y \text{Zn}_x \mid \text{K}_2\text{SO}_4 \quad \text{ZnSO}_4 \parallel \text{s.b.} \parallel \text{Zn}(\text{ClO}_4)_2 \mid \text{Zn}_x \text{Hg}_y$						
$[\text{Zn}(\text{ClO}_4)_2]_{\text{T}}$	Mixture		E.M.F. (mv)		$K \times 10^3$	
	$[\text{K}_2\text{SO}_4]_{\text{T}}$	$[\text{ZnSO}_4]_{\text{T}}$	d_1	d_2	d_1	d_2
0.03	0.03	0.03	14.5	15.15	2.38	2.19
0.02	0.04	0.02	14.95	16.5	3.22	2.12
0.02	0.05	0.02	17.00	18.8	2.81	2.24
0.04	0.04	0.04	15.2	15.8	2.31	2.21
0.02	0.06	0.02	18.6	20.8	2.60	2.01
0.03	0.06	0.03	7.5	18.8	2.48	2.13
0.02	0.07	0.02	20.7	22.7	2.24	2.81
0.03	0.07	0.03	18.2	19.8	2.28	2.08
Mean	2.54	2.10

TABLE V — CELL 'e'

$\text{Hg} \mid \text{Hg}_2\text{SO}_4 \quad \text{K}_2\text{SO}_4 \parallel \text{salt bridge} \parallel \text{K}_2\text{SO}_4 \quad \text{ZnSO}_4 \mid \text{Hg}_2\text{SO}_4 \quad \text{Hg}$						
$[\text{K}_2\text{SO}_4]_{\text{T}}$ unmixed.	Mixture		E.M.F. (mv)		$K \times 10^3$	
	$[\text{K}_2\text{SO}_4]_{\text{T}}$	$[\text{ZnSO}_4]_{\text{T}}$	e_1	e_2	e_1	e_2
0.06	0.03	0.03	2.4	2.6	5.93	4.87
0.06	0.04	0.02	1.5	1.5	6.39	6.39
0.07	0.05	0.02	1.5	1.5	4.56	4.56
0.08	0.04	0.04	2.6	3.0	4.95	3.49
0.08	0.06	0.02	1.05	1.2	7.23	4.74
0.09	0.06	0.03	1.80	2.3	4.47	1.67
0.09	0.07	0.02	1.1	1.3	5.24	3.30
0.10	0.07	0.03	1.55	1.9	4.65	1.97
0.10	0.08	0.02	1.05	1.25	4.06	1.62
Mean					5.28	3.62

TABLE VI — CELL 'I'

$\text{Hg}_y \text{ Zn}_x \left \begin{array}{cc} \text{K}_2\text{SO}_4 & \text{ZnSO}_4 \\ (c_1) & (c_2) \end{array} \right \text{Hg}_2\text{SO}_4 \left \text{Hg} \right.$					
$[\text{K}_2\text{SO}_4]_r$	$[\text{ZnSO}_4]_r$	e.m.f.	*E _o	**E _o	K × 10 ³
0.03	0.03	1.4926	1.3609	1.3601	4.02
0.04	0.02	1.4975	1.3626	1.3611	4.08
0.05	0.02	1.4975	1.3617	1.3599	3.84
0.04	0.04	1.4889	1.3612	1.3602	3.65
0.06	0.02	1.4974	1.3615	1.3591	3.65
0.06	0.03	1.4926	1.3615	1.3597	5.15
0.07	0.02	1.4975	1.3602	1.3581	3.62
0.07	0.03	1.4926	1.3617	1.3598	3.35
	Mean	1.3612	1.3597	3.92

*E_o is E_o calculated with a_{zn}^{2+} from cell d₁ (KCl) and $a_{\text{so}_4^{2-}}$ from cell c₁ (KCl).

**E_o is E_o calculated with a_{zn}^{2+} from cell d₂ (NH₄NO₃) and $a_{\text{so}_4^{2-}}$ from cell c₂ (NH₄NO₃).

DISCUSSION

In the cells 'a', 'b', 'd' and 'e' the elimination of liquid junction potential is assumed. The e.m.f. of the cells 'a' and 'd' is given by equation (1) and that of 'b' and 'e' is given by equation (2).

$$E = \frac{RT}{2F} \log_e \frac{a'_{\text{zn}^{2+}}}{a_{\text{zn}^{2+}}} \quad \dots \quad \dots \quad (1)$$

$$E = \frac{RT}{2F} \log_e \frac{a'_{\text{so}_4^{2-}}}{a_{\text{so}_4^{2-}}} \quad \dots \quad \dots \quad (2)$$

In the above equation (i) $a'_{\text{zn}^{2+}}$, (ii) $a_{\text{zn}^{2+}}$, (iii) $a'_{\text{so}_4^{2-}}$ and (iv) $a_{\text{so}_4^{2-}}$ stand respectively for the activity of (i) Zn^{2+} in solution of $\text{Zn}(\text{ClO}_4)_2$ in cell 'a' as well as 'd' (ii) Zn^{2+} in solutions of unmixed ZnSO_4 in cell 'a' as well as in solutions of mixtures of K_2SO_4 and ZnSO_4 in cell 'd', (iii) SO_4^{2-} in unmixed K_2SO_4 solutions in cell 'b' as well as in cell 'e' and (iv) SO_4^{2-} in solutions of unmixed ZnSO_4 in cell 'b' as well as in solutions of mixtures of K_2SO_4 and ZnSO_4 in cell 'e'. Zinc perchlorate⁴ and potassium sulphate⁶ solutions upto 0.1 molar concentration are completely dissociated. In this paper the activity coefficients of Zn^{2+} (assuming it to be the same as that of Ba^{2+} at the same ionic strength) and SO_4^{2-} ions have been calculated on the same assumption as in part 'I' of this series⁷ and are given by the following equations:

$$-\log_{10} f_{\text{zn}^{2+}} = 2.064 \sqrt{\mu} - 2.539 \mu + 1.20 \mu^{3/2} \quad \dots \quad (3)$$

$$-\log_{10} f_{\text{so}_4^{2-}} = 2.064 \sqrt{\mu} - 1.97 \mu + 0.93 \mu^{3/2} \quad \dots \quad (4)$$

Where μ = ionic strength.

On account of complete dissociation of $\text{Zn}(\text{ClO}_4)_2$ and K_2SO_4 in unmixed solutions, their ionic strengths are known and so $f_{\text{Zn}^{2+}}$ and $f_{\text{SO}_4^{2-}}$, in these cases, are found out from equations (3) and (4) respectively. Since activity is product of concentration of an ion and its activity coefficient, hence $a'_{\text{Zn}^{2+}}$ (activity of Zn^{2+} in $\text{Zn}(\text{ClO}_4)_2$ solutions in cell 'a' and 'd') and $a'\text{SO}_4^{2-}$ (activity of SO_4^{2-} in K_2SO_4 solutions in cell 'b' and unmixed K_2SO_4 solutions in cell 'e') are found out. With the help of equations (1) and (2) $a_{\text{Zn}^{2+}}$, (activity of Zn^{2+}) and $a_{\text{SO}_4^{2-}}$ (activity of SO_4^{2-}) in ZnSO_4 solution in the cells 'a' and 'b' and in solution of mixtures of K_2SO_4 and ZnSO_4 in cells 'd' and 'e' are found out.

The e.m.f. of the cell 'c' as well as that of cell 'f' is given by the equation:

$$E = E_0 - \frac{RT}{2F} \log_e a_{\text{Zn}^{2+}} a_{\text{SO}_4^{2-}} \quad \dots \quad (5)$$

Let us consider cell 'c'. For each concentration of zinc sulphate, investigations were made with cell 'a', 'b' and 'c'. If liquid junction potential has been eliminated and if assumptions about activity coefficients are correct (as explained in the previous paragraph) then $a_{\text{Zn}^{2+}}$ and $a_{\text{SO}_4^{2-}}$ for any concentration required in 'c' will be given by cells 'a' and 'b' (with either bridge) respectively and hence E_0 can be found out from cell 'c' corresponding to both the bridges. Whatever applies to the cells 'a', 'b' and 'c' will apply, with minor changes to cells 'd', 'e' and 'f'. The value of E_0 , calculated as above, is given in the third and fourth columns of table III and fourth and fifth columns of table VI. The value of normal electrode potential for $\text{Zn}_x\text{Hg}_y \mid \text{Zn}^{2+}$ from the work of Robinson and Stokes⁸ at 35°, comes to 0.7614 volt and that of $\text{Hg} \mid \text{Hg}_2\text{SO}_4 \mid \text{SO}_4^{2-}$ at 35°, to -0.6025 from our work⁶. Hence, E_0 for the type of the cells 'e' and 'f' comes to 1.3639. Let us once again confine our attention to cell 'c'. In column '3' of Table III values of E_0 have been calculated with $a_{\text{Zn}^{2+}}$ and $a_{\text{SO}_4^{2-}}$ in ZnSO_4 solution found, respectively from the cells of the types (a) and (b) having saturated KCl as salt bridge and in column '4' from cells having saturated NH_4NO_3 as salt bridge. In spite of the liquid junction potential having been taken to be zero and approximate nature of assumptions made, the average value of E_0 obtained from column '3' (KCl bridge) comes to 1.360. The same is the case with column '4' (NH_4NO_3 bridge). Both are 4 m.v. below the standard value of 1.3639 or say 1.364. The values of E_0 , both in columns '3' and '4', go on decreasing with increase in concentration of ZnSO_4 . If $*E_0$ (column '3') and $**E_0$ (column '4') are plotted against \sqrt{c} , where 'c' is the stoichiometric concentration of ZnSO_4 , both $*E$ and $*E_0$ and $**E_0$ come to 1.3624 when $C=0$. This value is about 1.5 m.v. lower than the standard value. Let us now consider cell 'f'. The mean value of $*E_0$ comes to 1.361 (3 m.v. lower than the standard value) and $**E_0$ to 1.360 i.e. about 4 m.v. lower than the standard value. As the variation of E_0 in cell 'f' is not in any definite order, it is not possible to extrapolate the values. From these results we can see that the assumptions made by us regarding activity coefficient of single ion and liquid junction potential, though rough, are fairly accurate for many purposes.

The cells studied also throw light on the formation of the complex $\text{Zn}(\text{SO}_4)_2^{2-}$. If α is the degree of dissociation of ZnSO_4 to Zn^{2+} and SO_4^{2-} and β is the degree of association forming $\text{Zn}(\text{SO}_4)_2^{2-}$, then the e.m.f. of the cell 'a' would be given by the equation (6) and that of cell 'b' by (7).

$$E = \frac{RT}{2F} \log_e \frac{Cf'_{2+}}{\alpha cf_{2+}} = \frac{RT}{2F} \log_e \frac{f'_{2+}}{\alpha f_{2+}} \quad \dots \quad (6)$$

$$E = \frac{RT}{2F} \log_e \frac{Cf'_{2-}}{C(\alpha - \beta)f_{2-}} = \frac{RT}{2F} \log_e \frac{f'_{2-}}{(\alpha - \beta)f_{2-}} \quad \dots \quad (7)$$

In equation (6) f'_{2+} stands for activity coefficient of Zn^{2+} in $\text{Zn}(\text{ClO}_4)_2$ solution and f_{2+} for activity coefficient of Zn^{2+} in ZnSO_4 solutions. In equation (7) f'_{2-} stands for activity coefficient of SO_4^{2-} in K_2SO_4 solution and f_{2-} for activity coefficient of SO_4^{2-} in ZnSO_4 solutions. As explained earlier f'_{2+} and f'_{2-} are calculated straight off from the known concentration of $\text{Zn}(\text{ClO}_4)_2$ and K_2SO_4 with the help of equations (3) and (4). For any concentration of ZnSO_4 used in cell 'a' the value of αf_{2+} is found from equation (6). An arbitrary value is now given to α and the corresponding value of μ , is found from the equation, $\mu = 4 - \alpha C$ where 'C' is stoichiometric concentration. This μ with the use of equation (3) gives a value of f_{2+} . If the product of arbitrary α and f_{2+} found therefrom is different from αf_{2+} found from equation (6), then α is altered till the product of α and f_{2+} found therefrom equals αf_{2+} from equation (6). It may be mentioned that $\mu = 4 - \alpha C$, even when complex of the type $\text{M}(\text{SO}_4)_2^{2-}$ is formed as shown on page 37 of part I of this series⁷. In such cells of 'a' and 'b' types which have same $[\text{SO}_4]_T$ the values of α and μ found in cell 'a' from equation (6) can be taken to be those of cell 'b' also. So in equation (7) f_{2-} can be calculated from equation (4) leaving one unknown i.e. β . On calculation it is found that ' β ' is negative in all the solutions of ZnSO_4 in cell 'b'. This means that (i) upto 0.1 M $\text{Zn}(\text{SO}_4)_2^{2-}$ is not formed in zinc sulphate solution, (ii) our assumptions are not accurate enough to give $\beta = 0$ and (iii) there is some systematic error possibly due to l.j.p. Similar equations are developed for the cells 'd' and 'e'. On similar analysis it is found that in solutions of mixtures of ZnSO_4 and K_2SO_4 also, the value of β comes to be negative and that $\text{Zn}(\text{SO}_4)_2^{2-}$ is not formed. In view of this, earlier findings in paper 'I' of this series regarding the existence of $\text{Cd}(\text{SO}_4)_2^{2-}$ shall have to be reexamined.

The next problem which is tackled is that of the dissociation constant (K) of ZnSO_4 i.e.

$$K = \frac{a_{\text{Zn}^{2+}} \times a_{\text{SO}_4^{2-}}}{[\text{ZnSO}_4]} \quad \dots \quad (8)$$

It is possible to calculate the value of 'K' from each of the six cells independently of other cells. Let us take cell 'a'. As explained in the previous paragraph, in any solution of zinc sulphate α , μ and f_{2+} are found from cell 'a' and equation (6). Hence f_{2-} can also be found out from equation (4). The equation (8) reduces itself to

$$K = \frac{\alpha^2 f_{2+} f_{2-}}{(1 - \alpha)} \quad \dots \quad (9)$$

7. This *Journal*, 1962, **39**, 33.

8. *Trans. Farad. Soc.*, 1940, **36**, 740.

We can calculate 'K' since we have the values of all the quantities on the right hand side. The values of 'K' are given in Table I, both for KCl and NH_4NO_3 bridges. As no $\text{Zn}(\text{SO}_4)_2^{2-}$ is formed, the e.m.f. of the cell 'b' is given by the equation:

$$E = \frac{RT}{2F} \log_{10} \frac{f'_{2-}}{\alpha f'_{2+}} \quad \dots \quad (10)$$

With cell 'b' and equation (10) we find out the value of α , μ and f_{2-} , by a process, similar to that applied in cell 'a' and equation (6). Since μ is known f_{2+} is found from equation (3) and 'K' can be calculated with the help of equation (9). The values of K, both when KCl and when NH_4NO_3 bridges are used, are given in Table II. In cell 'c' assuming that $E_0 = 1.3639$ volts, we get the correct value of $a_{\text{Zn}^{2+}} \times a_{\text{SO}_4^{2-}}$ in any solution of ZnSO_4 , from the equation (5). An arbitrary value is now given to ' α ' and the corresponding ionic strength is calculated. With this ' μ ' the values of f_{2+} and f_{2-} are found from equations (3) and (4) and the corresponding value of $\alpha^2 C^2 f_{2+} f_{2-}$ is calculated. If it differs from $a_{\text{Zn}^{2+}} \times a_{\text{SO}_4^{2-}}$, calculated from equation (5), then ' α ' is altered till the two agree. Thus we get correct values of α , f_{2+} and f_{2-} . The value of 'K' is calculated with the help of equation (9) and are given in column '5' of Table III. It may be pointed out that no liquid junction potential comes in, in this approach. In cell 'd' the concentration of Zn^{2+} in solutions of mixtures of K_2SO_4 and ZnSO_4 is given by $[\text{Zn}^{2+}] = \alpha [\text{ZnSO}_4]_T$. In cell 'e' the concentration of SO_4^{2-} is given by $[\text{SO}_4^{2-}] = [\text{K}_2\text{SO}_4]_T + \alpha [\text{ZnSO}_4]_T$. The rest of the process for calculating the values of 'K' in cells 'd' and 'e' is the same as in the case of cells 'a' and 'b'. The calculated values are given in columns '6' and '7' of both tables IV and V. The process for calculating the values of 'K' in cell 'f' is similar to that of cell 'c' except that the value of $a_{\text{Zn}^{2+}} \times a_{\text{SO}_4^{2-}}$ found from the cell 'f', with the help of equation (5), is compared with the value of $\alpha [\text{ZnSO}_4]_T \times \{[\text{K}_2\text{SO}_4]_T + \alpha [\text{ZnSO}_4]_T\} \times f_{2+} \times f_{2-}$ and ' α ' is altered till the two have the same value. The values of 'K' are given in the last column of Table VI. All the cells give values of 'K' of the same order. Cells of the types 'c' and 'f' have no liquid junction potential. Hence they should give more reliable values. Values of 'K' either in cell of the type 'c' or 'f' are not constant. The assumptions about activity coefficient which are correct at zero or very low concentrations become more and more inaccurate as the concentration increases and they might be responsible for the lack of constancy. The mistake made may be rectified if the value of 'K' is extrapolated to zero concentration. The cell of the type 'f' on account of its higher ionic strength and on account of the variation in ionic strength being not much, is not suitable for extrapolation, whereas the cell of the type 'c' is suitable for extrapolation. The value of 'K' obtained from cell 'c' by extrapolating the plot of 'K' against \sqrt{c} , when $c=0$, comes to 7.5×10^{-3} . This may be taken to be the most accurate value of 'K'. When we are not able to get a cell reversible to cation, then we can not get a cell of the type 'c'. The value of K can still be studied with cells of the type 'b' or 'e'. The cell of the type 'c' is not preferred because it is not suitable for extrapolation. The cell 'b' has the advantage that the values can be extrapolated to zero concentration. The extrapolated value of 'K' of zinc sulphate (cell b—Table II) comes to 8.8×10^{-3} with KCl bridge and 6.4×10^{-3} with NH_4NO_3 bridge. Either value is not much different from 7.5×10^{-3} obtained from cell 'c'. The value found by Davies at 18° is 5.3×10^{-3} and that found by Owen and Curry is 4.9×10^{-3} at 25° .