742. *Thermodynamics of Ion Association. Part IV.*[1] *Magnesium and Zinc Sulphates.*

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Thermodynamic equilibrium constants for the association in aqueous solution of magnesium and zinc ions with the sulphate ion have been determined by a precise e.m.f. method at various temperatures between 0° and 45°. ΔG, ΔH, and ΔS for the reaction $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$ have been calculated and these are discussed.

In a previous paper[1] the thermodynamic properties for the association between the thallous ion and univalent anions have been determined from solubilities and conductivities. We have now investigated the association between similarly charged ions of higher valency type. Since the bisulphate ion is incompletely dissociated and its dissociation constant is known with considerable certainty over a range of temperature,[2] the bivalent metal sulphates can be studied by using the cell H_2,Pt | MSO_4,HCl | AgCl–Ag. Jones and Monk[3] with a similar cell studied magnesium sulphate and obtained e.m.f.s to within 100 μv at temperatures from 20° to 35°. In order to obtain reliable estimates of the association constants, however, very precise measurements are required since an error of $\pm$100 μv in the e.m.f.'s would produce a variation of 10—20% in the association constants.[3] Measurements have been made on similar cells with the refined apparatus described in part V.[2]

Experimental

" AnalaR " magnesium and zinc sulphates were recrystallised three times from conductivity water and dried at 110°. Small samples in weighing tubes having ground glass caps were rendered anhydrous by heating to constant weight in a muffle furnace at 350° to 420°, then dropped into hydrochloric acid solutions of known molality; the solutions were made up by

[1] Part III, Nair and Nancollas, *J.*, 1957, 318.
[2] Nair and Nancollas, *J.*, in the press.
[3] Jones and Monk, *Trans. Faraday Soc.*, 1952, **48**, 929.

weight with conductivity water. The stock solutions were analysed for sulphate by precipitation as barium sulphate [4] and agreement was within 0·03% of the calculated concentrations. The preparation of hydrochloric acid, standardisation of electrodes, and experimental technique will be described later.[2] Experiments were usually made from 0° to 25° and a new cell filling was used for measurements from 25° to 45°. The e.m.f.s obtained at the same temperature with different fillings never varied by more than 30 μv.

Results and Discussion

The e.m.f. of the cell H_2,Pt | HCl(m_1), MSO_4(m_2) | AgCl–Ag is given by

$$E = E^\circ - k \log a_{H^+} a_{Cl^-}$$

or

$$-\log m_{H^-} = (E - E^\circ)/k + \log m_1 + \log \gamma_{H^+} \gamma_{Cl^-}$$

where m represents molality, γ activity coefficient, and $k = 2{\cdot}3026\, \boldsymbol{RT/F}$. Assuming that the only association taking place is that between the bivalent ions, we find the concentrations of ion species $m_{HSO_4^-} = m_1 - m_{H^+}$, $m_{M^{2+}} = m_{HSO_4^-} + m_{SO_4^{2-}}$, and $m_{MSO_4} = m_2 - m_{M^{2+}}$. The ionic strength, $I = m_1 + 4m_2 - 2m_{HSO_4} - 4m_{MSO_4}$, and the dissociation constant of the bisulphate ion, $k_2 = a_{H^+} a_{SO_4^{2-}}/a_{HSO_4^-}$, has the values obtained previously.[1] The association constant, $K = a_{MSO_4}/a_{M^{2+}} a_{SO_4^{2-}}$, was obtained by successive approximations of I by use of Davies's modified form of the Debye–Hückel equation [5]

$$\log \gamma_z = Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - CI] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $C = 0{\cdot}2$. The results are given in Table 1 together with the mean values of K at each temperature.

Dunsmore and James [6] obtained a value $K = 161$ kg. mole^{-1} for magnesium sulphate at 25° from conductivity measurements. Jones and Monk [3] have recalculated these data allowing for a drift in K with concentration and give $K = 185$ kg. mole^{-1}. Robinson and Stokes [7] have re-analysed Dunsmore and James's results using the Bjerrum critical distance for a 2 : 2 electrolyte, $a_i = 14{\cdot}28$ Å, in the activity-coefficient expression and obtained $K = 201{\cdot}6$ kg. mole^{-1}. Jones and Monk [3] have reported a value of 227 kg. mole^{-1} from e.m.f. measurements: the new value being used for k_2,[2] this is reduced to 212 kg. mole^{-1}. Our value at 25°, 179, is in general agreement with these. At 18°, the interpolated value 155·5 kg. mole^{-1} agrees with that of Davies,[8] 164 kg. mole^{-1}, from conductivity measurements. The conductivity of zinc sulphate solutions has been measured by Owen and Gurry [9] who derived $K = 204$ kg. mole^{-1} at 25°. Robinson and Stokes [7] have recalculated these data by the method outlined for magnesium sulphate and obtained $K = 227$ kg. mole^{-1}. At 0° the cryoscopic measurements of Brown and Prue [10] give $K = 111$ kg. mole^{-1} for both magnesium sulphate and zinc sulphate which may be compared with the present values of 92 and 121 kg. mole^{-1} respectively.

The heats of formation, ΔH, have been obtained from the linear plots shown in the Figure of log K against T^{-1} with use of least squares (Table 2).

Davies's expression for activity coefficients with $C = 0{\cdot}2$ in eqn. (1) corresponds to a distance of closest approach of the ions, q, of about 4·3 Å. There is a considerable latitude in the choice of values for this parameter and the subject has received much attention.[10,11,12] Beevers and Lipson's [13] X-ray data for copper sulphate were used by

[4] Vogel, " A Text Book of Quantitative Analysis," Longmans, London, 1947.
[5] Davies, *J.*, 1938, 2093.
[6] Dunsmore and James, *J.*, 1951, 2925.
[7] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955.
[8] Davies, *Trans. Faraday Soc.*, 1927, **23**, 351.
[9] Owen and Gurry, *J. Amer. Chem. Soc.*, 1938, **60**, 3074.
[10] Brown and Prue, *Proc. Roy. Soc.*, 1955, *A*, **232**, 320.
[11] Guggenheim, *Discuss. Faraday Soc.*, 1957, No. 24, 53.
[12] Davies, Otter, and Prue, *ibid.*, p. 103.
[13] Beevers and Lipson, *Proc. Roy. Soc.*, 1934, *A*, **146**, 570.

Brown and Prue [10] to show that, at least for this salt, a q value of about 4 Å was reasonable. Guggenheim [11] favoured larger values of q of the order of 10 Å and suggested that for 2 : 2 electrolytes a value of $C = 2{\cdot}0$ corresponding to $q \sim 9$ Å would be more appropriate. The position in the mixed electrolytes of the present work is complicated since the significance of the q value is uncertain. When recalculations are made with $C = 2{\cdot}0$ in the expression for the activity coefficients of bivalent ions, K for magnesium sulphate at 25° varies by 20—30% in the range of ionic strengths studied. As can be seen in Table 1,

TABLE 1. *E.m.f. measurements.*

Magnesium sulphate

No.	10^3m_1	10^3m_2	No.	10^3m_1	10^3m_2	No.	10^3m_1	10^3m_2
1	5·522	3·619	4	6·170	5·333	7	3·929	34·786
2	7·127	5·222	5	4·392	38·497	8	6·108	21·853
3	7·575	5·148	6	3·652	16·727	9	4·914	19·341

No.	$(E - E°)$	10^3I	$10^3m_{HSO_4^-}$	$10^3m_{M^{2+}}$	$10^3m_{MSO_4}$	K	K (mean)
			Temp. 0°				
1	0·25226	17·59	0·347	3·274	0·345	100	
2	0·24158	24·56	0·567	4·641	0·581	94·4	
3	0·23867	24·66	0·590	4·575	0·573	102	
4	0·24843	24·37	0·512	4·771	0·562	89·2	
8	0·25602	75·46	1·256	17·971	3·882	78·5	
9	0·26542	66·34	0·952	15·846	3·495	82·9	92·0
			Temp. 20°				
1	0·27210	16·73	0·602	3·184	0·435	149	
2	0·26082	22·94	0·947	4·426	0·796	169	
3	0·25771	23·23	0·987	4·401	0·747	163	
4	0·26813	22·20	0·847	4·430	0·903	(183)	160
			Temp. 25°				
1	0·27704	16·46	0·656	3·143	0·475	171	
2	0·26566	22·66	1·032	4·399	0·824	182	
3	0·26249	22·97	1·078	4·387	0·761	188	
4	0·27313	22·00	0·928	4·223	0·911	190	
5	0·30709	101·70	1·889	25·337	13·160	177	
6	0·30838	50·78	1·131	12·279	4·448	166	179
			Temp. 30°				
5	0·31265	94·95	1·981	23·618	14·879	227	
6	0·31406	47·25	1·197	11·451	5·276	224	
7	0·31763	88·46	1·728	21·916	12·870	216	222
			Temp. 35°				
1	0·28706	15·68	0·789	3·027	0·592	247	
2	0·27547	21·71	1·234	4·265	0·957	243	
3	0·27218	22·05	1·284	4·252	0·896	235	
4	0·28338	21·27	1·130	4·358	0·975	(225)	
5	0·31951	92·80	2·128	23·142	15·355	247	
6	0·32030	45·54	1·298	11·084	5·643	257	
7	0·32410	83·75	1·838	20·809	13·977	258	248
			Temp. 40°				
5	0·32622	90·90	2·251	22·862	15·635	(260)	
6	0·32657	43·75	1·394	10·944	5·783	272	
7	0·33055	80·22	1·933	20·130	14·656	290	281
			Temp. 45°				
1	0·29734	15·22	0·942	2·986	0·633	294	
2	0·28548	20·90	1·452	4·190	1·032	295	
3	0·28208	21·51	1·509	4·194	0·954	276	
4	0·29379	20·61	1·336	4·284	1·049	(265)	
5	0·33316	87·41	2·384	21·944	16·550	303	
6	0·33288	42·12	1·385	10·393	6·334	332	
7	0·33683	73·96	2·020	18·505	16·281	374	312

Zinc sulphate

No.	10^3m_1	10^3m_2	No.	10^3m_1	10^3m_2	No.	10^3m_1	10^3m_2
1	7·527	3·571	3	7·664	4·200	5	6·373	4·554
2	6·406	4·554	4	5·328	3·934	6	5·294	4·825

TABLE 1. (*Continued.*)

No.	$(E - E°)$	$10^3 I$	$10^3 m_{HSO_4^-}$	$10^3 m_{M^{2+}}$	$10^3 m_{MSO_4}$	K	K (mean)
			Temp. 0°				
1	0·23783	19·47	0·438	3·205	0·366	120	
2	0·24600	21·38	0·458	3·971	0·583	127	
3	0·23745	21·58	0·506	3·736	0·464	117	
4	0·25419	18·63	0·354	3·500	0·434	113	
5	0·26425	21·39	0·457	3·981	0·573	124	
6	0·25509	21·20	0·405	4·177	0·648	124	121
			Temp. 15°				
3	0·25130	20·53	0·724	3·587	0·613	189	
4	0·26896	17·61	0·512	3·328	0·606	184	
5	0·26068	20·35	0·661	3·828	0·726	182	
6	0·27008	20·14	0·588	4·002	0·823	183	185
			Temp. 20°				
3	0·25605	20·04	0·833	3·513	0·687	223	
4	0·27409	17·28	0·598	3·283	0·651	211	
5	0·26114	19·89	0·765	3·760	0·794	215	
6	0·27531	19·78	0·688	3·962	0·863	234	220
			Temp. 25°				
1	0·26086	17·96	0·792	3·006	0·565	249	
2	0·27032	19·74	0·842	3·754	0·800	225	
3	0·26074	19·83	0·907	3·495	0·706	240	
4	0·27906	16·95	0·650	3·232	0·702	241	
5	0·27053	19·57	0·831	3·711	0·843	240	
6	0·28027	19·14	0·740	3·843	0·982	248	240
			Temp. 35°				
1	0·27049	17·53	0·964	2·984	0·587	288	
2	0·28028	19·08	1·019	3·674	0·880	278	
3	0·27020	19·09	1·084	3·396	0·804	314	
4	0·28930	16·46	0·796	3·178	0·756	288	
5	0·28043	18·77	1·003	3·611	0·943	307	
6	0·29068	18·54	0·904	3·773	1·052	298	295
			Temp. 45°				
1	0·27995	16·89	1·118	2·892	0·679	(394)	
2	0·29047	18·63	1·214	3·648	0·906	319	
3	0·27991	18·65	1·283	3·378	0·822	362	
4	0·29967	15·92	0·948	3·120	0·814	349	
5	0·29062	18·32	1·197	3·593	0·961	345	
6	0·30141	18·17	1·092	3·780	1·045	317	338

TABLE 2. *Thermodynamic properties.*

Reaction	ΔH (kcal. mole^{-1})	ΔG_{298} (kcal. mole^{-1})	ΔS (calc. deg.$^{-1}$ mole^{-1})
Mg^{2+}, SO_4^{2-}	4·84	−3·07	26·2
Zn^{2+}, SO_4^{2-}	4·01	−3·25	24·4

however, the use of $C = 0{\cdot}2$ yields K values which show no such tendency to drift with ionic strength.

The entropy of association can be written

$$\Delta S = \Delta S_g + \Delta S_{hyd}(MSO_4) - \Delta S_{hyd}(M^{2+}) - \Delta S_{hyd}(SO_4^{2-}) \quad . \quad . \quad . \quad (2)$$

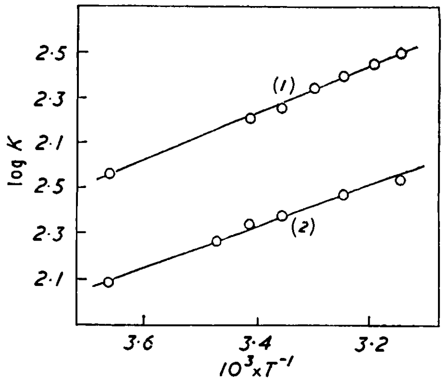
where ΔS_g and ΔS_{hyd} represent gaseous and hydration entropies respectively. $\Delta S_{hyd}(M^{2+})$ and $\Delta S_{hyd}(SO_4^{2-})$ were obtained from the known gaseous and standard entropies,[14] and

$$\Delta S_g = S_{trans}(MSO_4) - S_{trans}(M^{2+}) - S_{trans}(SO_4^{2-}) - S_{rot}(SO_4^{2-}) + S_{rot}(MSO_4)$$

$S_{trans}(MSO_4)$ and $S_{rot}(MSO_4)$ were calculated by the methods described elsewhere [1] with the bond lengths and atomic radii given by Pauling.[15] Values of $\Delta S_{hyd}(MSO_4)$ were

[14] Latimer, " Oxidation Potentials," Prentice-Hall, New York, 1952.
[15] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1939.

obtained by substitution of the calculated entropies in eqn. (2) and the data are summarised in Table 3 which also includes some values for ion pairs formed between univalent ions. The considerably higher $-\Delta S_{hyd}(MX)$ values for the bivalent sulphates possibly



Plots of log K *against* T^{-1} *for* (1) *magnesium sulphate and* (2) *zinc sulphate.*

TABLE 3. *Thermodynamic properties.*

Ion pair	S_g (MX) (cal. deg.$^{-1}$ mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	$S°$ (MX) (cal. deg.$^{-1}$ mole^{-1})	$-\Delta S_{hyd}$ (MX) (cal. deg.$^{-1}$ mole^{-1})
$MgSO_4$	68·8	26·2	3·1	65·7
$ZnSO_4$	70·9	24·4	2·8	68·1
TlCl	60·9	−1·7	41·9	19·0
TlBr	62·8	−4·2	45·5	17·3

reflect a smaller degree of charge neutralisation accompanying their formation than in the case of the thallous ion pairs which are usually considered to be more covalent.

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