791. *Thermodynamics of Ion Association. Part VI.*[1] *Some Transition-metal Sulphates.*

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E.m.f.s of cells of the type $H_2,Pt|MSO_4,HCl|AgCl|Ag$ have been measured by a precision method at temperatures from 0° to 45° and thermodynamic association constants are derived for the formation of $MnSO_4$, $CoSO_4$, and $NiSO_4$. ΔH, ΔG, and ΔS are evaluated for the reaction $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$, and these are discussed.

THE stability of transition-metal complexes has been discussed by Irving and Williams[2] who found that for a number of neutral ligands and anions of weak acids, the association constants lie in the sequence Mn $<$ Fe $<$ Co $<$ Ni $<$ Cu $>$ Zn. Owing to the lack of temperature-coefficient data, however, all such discussions involve the assumption that the free-energy change is dominated by the heat term and that changes in the entropy of

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[1] Part V, Nair and Nancollas, *J.*, 1958, 4144.
[2] Irving and Williams, *J.*, 1953, 3192.

association may be neglected. Both the heat and the entropy term should be considered, and the present investigation extends the available data for sulphates[3] to those of manganese, cobalt, and nickel. Cells of the type described previously[1,3]

$$\text{H}_2,\text{Pt} \mid \text{HCl},\text{MSO}_4 \mid \text{AgCl} \mid \text{Ag}$$

have been used, and e.m.f.s have been measured at various temperatures between 0° and 45°.

EXPERIMENTAL

"AnalaR" manganese, cobalt, and nickel sulphates were recrystallised three times from conductivity water. Manganese sulphate has a maximum solubility at 54—55° and solutions prepared at this temperature were evaporated to about two-thirds of the original volume before crystallisation. Recrystallised manganese and cobalt sulphates were converted into the anhydrous forms and stock solutions were prepared as described previously:[3] analysis for sulphate by precipitation as barium sulphate agreed to within 0·03% of the calculated concentrations. Since anhydrous nickel sulphate dissolves in water only with difficulty, stock solutions were prepared from the hydrated salt and analysed for nickel by precipitation as the dimethylglyoxime.[4] Duplicated estimations agreed to 0·02%. The apparatus and experimental technique have been described previously.[1] E.m.f. readings were constant to within 20 μv.

RESULTS AND DISCUSSION

The concentration of hydrogen ions, m_{H^+}, in the cell

$$\text{H}_2,\text{Pt} \mid \text{HCl}(m_1),\ \text{MSO}_4(m_2) \mid \text{AgCl} \mid \text{Ag}$$

can be expressed by

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

where γ represents activity coefficient, m molalities, and $k = 2{\cdot}3026\,\boldsymbol{RT/F}$. Using equations for the concentrations of ionic species: $m_{\text{HSO}_4^-} = m_1 - m_{\text{H}^+}$, $m_{\text{M}^{2+}} = m_{\text{HSO}_4^+} + m_{\text{SO}_4^{2-}}$, and $m_{\text{MSO}_4} = m_2 - m_{\text{M}^{2+}}$, and the dissociation constant of the bisulphate ion, $k_2 = a_{\text{H}^+}a_{\text{SO}_4^{2-}}/a_{\text{HSO}_4^-}$, we calculated the thermodynamic association constants $K = a_{\text{MSO}_4}/a_{\text{M}^{2+}}a_{\text{SO}_4^{2-}}$ by the method described previously.[3] Activity coefficients were obtained from Davies's modification of the Debye–Hückel equation[5]

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

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

The association constants at 25°, $K(\text{CoSO}_4) = 230$ kg. mole^{-1} and $K(\text{NiSO}_4) = 211$ kg. mole^{-1}, are lower than the corresponding values 294 and 250 obtained by Money and Davies[6] from conductivity measurements: for manganese sulphate, however, our value, 181 kg. mole^{-1} is in good agreement with James's conductimetric value,[7] 192 kg. mole^{-1}. At 0°, $K(\text{NiSO}_4) = 121$ kg. mole^{-1} and $K(\text{CoSO}_4) = 172$ kg. mole^{-1} can be compared with the cryoscopic values, 125 and 111 respectively, obtained by Brown and Prue.[8] The CoSO_4 values are rather different and it is noteworthy that the cryoscopic results show small systematic deviations for all the curves in the case of cobalt sulphate.[8]

Heats of association have been derived by use of least squares from the linear plots of $\log K$ against T^{-1} shown in the Figure. Values of ΔG, ΔH, and ΔS together with mean deviations (calculated by least squares on the assumption that the deviations of the points from the straight lines in the Figure are themselves a measure of the error in ΔH), are

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[3] Nair and Nancollas, Part IV, *J.*, 1958, 3706.

[4] Vogel, " A Text Book of Quantitative Analysis," Longmans, London, 1947.

[5] Davies, *J.*, 1938, 2093.

[6] Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609.

[7] James, Ph.D. Thesis, London, 1947.

[8] Brown and Prue, *Proc. Roy. Soc.*, 1955, *A*, **232**, 320.

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

Manganese sulphate

Expt.	1	2	3	4	5
10^3m_1	3·777	6·122	8·679	3·903	2·824
10^3m_2	2·648	5·334	4·425	7·254	12·948

Temp.	Expt.	$(E - E°)$	10^3I	$10^3m_{HSO_4^-}$	$10^3m_{M^{2+}}$	$10^3m_{MSO_4}$	K	K (mean)
0°	2	0·24873	23·95	0·504	4·707	0·627	101	
	1	0·26916	13·15	0·194	2·423	0·225	103	
	3	0·23188	23·48	0·590	3·992	0·433	101	103
	4	0·27099	27·98	0·415	6·205	1·049	101	
	5	0·28891	43·53	0·435	10·409	2·539	107	
10°	1	0·27947	12·75	0·256	6·205	1·049	135	
	2	0·25853	23·21	0·651	10·409	2·539	129	
	3	0·24097	22·97	0·761	2·373	0·275	122	129
	4	0·28185	27·13	0·539	4·602	0·732	123	
	5	0·30077	41·75	0·555	3·945	0·480	134	
20°	1	0·29004	12·53	0·346	2·350	0·298	158	
	2	0·26863	22·43	0·852	4·505	0·839	165	
	3	0·25024	22·22	0·988	3·884	0·541	154	160
	4	0·29306	25·97	0·704	5·858	1·396	161	
	5	0·31331	40·21	0·720	9·734	3·214	161	
25°	1	0·29526	12·32	0·381	2·329	0·319	176	
	2	0·27359	22·10	0·927	4·455	0·879	181	
	3	0·25457	21·90	1·069	3·839	0·586	178	181
	4	0·29859	25·47	0·767	5·776	1·478	178	
	5	0·31919	38·79	0·770	9·372	3·576	193	
35°	1	0·30593	11·97	0·473	2·287	0·361	218	
	2	0·28391	21·54	1·136	4·427	0·907	204	
	3	0·26417	21·32	1·288	3·799	0·626	214	212
	4	0·31014	24·74	0·937	5·668	1·586	208	
	5	0·33217	37·63	0·932	9·192	3·756	218	
45°	1	0·31672	11·60	0·511	2·240	0·408	276	
	2	0·29427	20·68	1·333	4·307	1·037	265	
	3	0·27361	20·64	1·503	3·739	0·686	269	262
	4	0·32193	23·83	1·112	5·528	1·726	250	
	5	0·34552	36·56	1·094	8·975	3·973	251	

Cobalt sulphate

Expt.	1	2	3	4	5	6
10^3m_1	6·933	5·960	8·259	6·986	4·488	5·865
10^3m_2	4·177	3·360	6·079	7·369	4·061	5·850

Temp.	Expt.	$(E - E°)$	10^3I	$10^3m_{HSO_4^-}$	$10^3m_{M^{2+}}$	$10^3m_{MSO_4}$	K	K (mean)
0°	1	0·24193	20·12	0·444	3·522	0·655	178	
	2	0·24842	16·96	0·336	2·923	0·437	158	
	3	0·23494	26·75	0·675	4·958	1·121	179	
	4	0·24356	29·37	0·666	5·908	1·461	170	172
	5	0·26209	17·46	0·298	3·399	0·662	172	
	6	0·25076	23·86	0·489	4·746	1·104	174	
5°	1	0·24657	19·95	0·491	3·516	0·661	184	
	2	0·25314	16·77	0·369	2·890	0·470	177	
	3	0·23949	26·46	0·741	4·926	1·153	190	
	4	0·24818	28·82	0·733	5·820	1·549	185	185
	5	0·26710	17·27	0·329	3·370	0·691	188	
	6	0·25559	23·61	0·532	4·700	1·150	188	
15°	1	0·25628	19·65	0·658	3·509	0·668	200	
	2	0·26286	16·42	0·496	2·865	0·495	202	
	3	0·24899	25·98	0·988	4·934	1·145	201	
	4	0·25816	28·29	0·981	5·822	1·547	196	200
	5	0·27750	17·05	0·448	3·365	0·696	200	
	6	0·26573	23·13	0·721	4·678	1·172	205	
25°	1	0·26587	19·18	0·842	3·484	0·480	228	
	2	0·27283	16·06	0·640	2·850	0·510	226	
	3	0·25862	25·26	1·245	4·872	1·207	237	
	4	0·26831	27·52	1·236	5·726	1·643	231	230
	5	0·28815	16·91	0·590	3·403	0·658	(196)	
	6	0·27633	22·60	0·925	4·644	1·206	229	

TABLE 1. (*Continued.*)

Cobalt sulphate (contd.)

Temp.	Expt.	$(E - E^\circ)$	$10^3 I$	$10^3 m_{\mathrm{HSO_4^-}}$	$10^3 m_{\mathrm{M^{2+}}}$	$10^3 m_{\mathrm{MSO_4}}$	K	K (mean)
35°	1	0·27569	18·74	1·033	3·478	0·699	250	
	2	0·28267	15·70	0·786	2·829	0·531	260	
	3	0·26837	24·71	1·520	4·877	1·202	255	
	4	0·27869	26·90	1·512	5·735	1·634	247	253
	5	0·29875	16·31	0·720	3·309	0·752	253	
	6	0·28655	22·10	1·135	4·626	1·224	251	
45°	1	0·28571	18·40	1·237	3·490	0·687	271	
	2	0·29280	15·37	0·950	2·836	0·524	279	
	3	0·27839	24·19	1·793	4·876	1·203	284	
	4	0·28937	26·43	1·805	5·768	1·601	261	277
	5	0·30961	15·88	0·870	3·282	0·779	284	
	6	0·29722	21·56	1·352	4·586	1·264	286	

Nickel sulphate

Expt. ……	1	2	3	4	5	6	7	8
$10^3 m_1$ ……	6·469	5·356	4·545	2·771	3·252	6·096	4·866	10·656
$10^3 m_2$ ……	2·868	2·670	1·863	5·559	9·700	11·300	4·581	3·957

Temp.	Expt.	$(E - E^\circ)$	$10^3 I$	$10^3 m_{\mathrm{HSO_4^-}}$	$10^3 m_{\mathrm{M^{2+}}}$	$10^3 m_{\mathrm{MSO_4}}$	K	K (mean)
0°	1	0·24430	16·24	0·325	2·597	0·271	123	
	2	0·25289	14·52	0·263	2·430	0·240	117	
	3	0·25972	11·14	0·171	1·729	0·134	115	
	5	0·28069	33·64	0·413	7·833	1·867	122	121
	6	0·25187	40·63	0·810	9·040	2·260	128	
	7	0·25885	20·07	0·363	3·986	0·595	122	
10°	1	0·25369	15·85	0·421	2·552	0·316	157	
	2	0·26257	14·18	0·344	2·386	0·284	150	151
	3	0·26959	10·90	0·226	1·705	0·158	146	
15°	1	0·25840	15·64	0·477	2·533	0·335	174	
	2	0·26746	14·00	0·388	2·358	0·312	174	
	3	0·27454	10·78	0·256	1·687	0·176	170	
	4	0·30275	19·93	0·593	4·470	1·089	179	174
	5	0·29776	31·73	0·593	7·418	2·282	172	
	6	0·26737	38·23	1·148	8·617	2·683	176	
	7	0·27408	19·20	0·532	3·848	0·733	171	
25°	1	0·26797	15·20	0·606	2·480	0·388	228	
	2	0·27741	13·75	0·502	2·341	0·329	200	
	3	0·28460	10·57	0·335	1·677	0·186	195	
	4	0·31442	19·22	0·467	4·344	1·215	219	
	5	0·30968	30·52	0·750	7·183	2·517	208	211
	6	0·27828	37·04	1·437	8·437	2·863	207	
	7	0·28452	18·59	0·682	3·772	0·809	207	
	8	0·24321	17·94	1·133	3·373	0·584	227	
35°	1	0·27765	14·87	0·745	2·471	0·397	256	
	2	0·28737	13·37	0·620	2·313	0·357	239	
	3	0·29469	10·32	0·415	1·651	0·212	246	
	4	0·32636	18·73	0·580	4·278	1·281	247	247
	5	0·32190	29·54	0·912	7·026	2·674	239	
	6	0·28929	35·55	1·721	8·221	3·079	247	
	7	0·29488	17·94	0·832	3·686	0·895	256	
45°	1	0·28739	14·45	0·883	2·435	0·433	310	
	2	0·29754	13·06	0·746	2·301	0·369	274	
	3	0·30494	10·11	0·505	1·645	0·218	279	
	4	0·33857	18·19	0·701	4·206	1·353	284	289
	5	0·33430	28·24	1·072	6·769	2·931	294	
	6	0·30070	34·43	2·022	8·099	3·201	280	
	7	0·30581	17·35	0·994	3·622	0·959	305	

given in Table 2; data for the sulphates of magnesium, zinc,[3] and calcium [9] are included for comparison.

The entropy of association can be written in terms of gas and hydration entropies:

$$\Delta S = \Delta S_{\mathrm{g}} + \Delta S_{\mathrm{hyd}}(\mathrm{MSO_4}) - \Delta S_{\mathrm{hyd}}(\mathrm{M^{2+}}) - \Delta S_{\mathrm{hyd}}(\mathrm{SO_4{}^{2-}})$$

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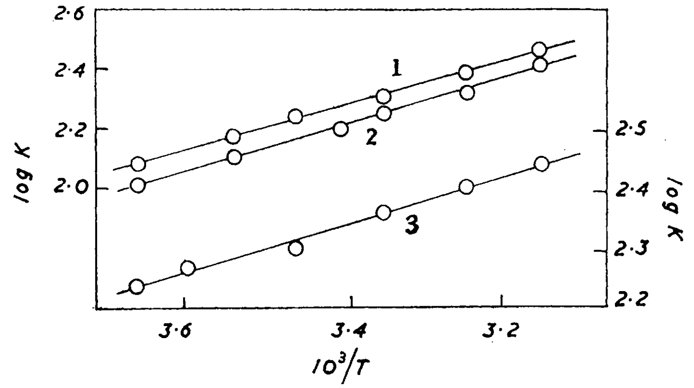
[9] Bell and George, *Trans. Faraday Soc.*, 1953, **49**, 619.

There is considerable uncertainty in the value for the standard entropy of the nickel ion. Latimer[10] quotes the Bureau of Standards' value, —38·1 cal. deg.$^{-1}$ mole^{-1}, but points out that such a low value cannot be accepted in comparison with $S°(Fe^{2+})$ and $S°(Cu^{2+})$ even though there may be considerable divergence in the multiplicity of the ground states.

Plots of log K *against* T^{-1} *for* (1) *nickel sulphate,* (2) *manganese sulphate* (*left-hand ordinates*), *and* (3) *cobalt sulphate* (*right-hand ordinate*).



Staveley and Randall[11] consider —23 cal. deg.$^{-1}$ mole^{-1} to be more reliable and we have used the latter value together with —22 cal. deg.$^{-1}$ mole^{-1} for the standard entropy of the cobalt ion.[11] $\Delta S_{hyd}(MSO_4)$, calculated as described previously,[3] is given in Table 3.

TABLE 2. *Thermodynamic properties.*

Reaction	ΔH (kcal. mole^{-1})	ΔG_{298} (kcal. mole^{-1})	ΔS cal. deg.$^{-1}$ mole^{-1})
$Mn^{2+} + SO_4^{2-}$	3·37 ± 0·31	−3·07 ± 0·02	22·6 ± 1·0
$Co^{2+} + SO_4^{2-}$	1·74 ± 0·16	−3·21 ± 0·02	16·6 ± 0·5
$Ni^{2+} + SO_4^{2-}$	3·31 ± 0·20	−3·16 ± 0·03	21·7 ± 0·7
$Zn^{2+} + SO_4^{2-}$	4·01 ± 0·55	−3·25 ± 0·02	24·4 ± 1·8
$Mg^{2+} + SO_4^{2-}$	4·84 ± 0·40	−3·07 ± 0·03	26·2 ± 1·3
$Ca^{2+} + SO_4^{2-}$	1·65 ± 0·20	−3·15 ± 0·03	16·1 ± 0·8

TABLE 3. *Thermodynamic properties.*

Ion pair	S_g (MSO_4) (cal. deg.$^{-1}$ mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	$S°(MSO_4)$ (cal. deg.$^{-1}$ mole^{-1})	$-\Delta S_{hyd}$ (MSO_4) (cal. deg.$^{-1}$ mole^{-1})	$r_{\pm}^{-1}$ (Å^{-1})
$MnSO_4$	70·1	22·6	6·7	63·4	1·28
$CoSO_4$	70·2	16·6	−1	71	1·35
$NiSO_4$	70·2	21·7	3	67	1·37
$ZnSO_4$	70·3	24·4	3·0	67·3	1·39
$MgSO_4$	68·2	26·2	2·1	66·1	1·52
$CaSO_4$	69·5	16·1	7·0	62·5	1·01

An attempt to correlate the thermodynamic data with various properties of the metal ions such as electronegativity and ionization potential showed no obvious relationship. The Irving–Williams order of stability[2] observed with a large number of neutral ligands and anions of weak acids, will be expected to hold only when the ligands interact with protons more strongly than does water. The association constants for the sulphate ion pairs are closely similar and the proton complex with this ligand is less stable than the H_3O^+ ion. Indeed, with cobalt and nickel sulphates, the Irving–Williams order is reversed.

The most frequently applied correlation involves the entropy of association and some function of the radii of the ions. It is important in this connection to consider, if possible,

[10] Latimer, " Oxidation Potentials," Prentice-Hall, New York, 1952.

[11] Staveley and Randall, *Discuss. Faraday Soc.*, 1958, **26**, 157.

only the hydration entropies of the complex ions when applying these methods since, in general, complex ions will contain different translational and rotational terms. Also the variable $\Delta S_{\text{hyd}}(\text{M}^{2+})$ term should be eliminated since this itself varies linearly with r_+^{-1}. Inspection of Table 3 indicates that there is a general increase in $-\Delta S_{\text{hyd}}(\text{MSO}_4)$ with r_+^{-1} in going from manganese to nickel and zinc but the value for cobalt appears to be anomalous. Until more reliable estimates are available for the standard entropies of nickel and cobalt ions, it is not possible to carry the comparison any further.

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