420. *Thermodynamics of Ion Association. Part VII.*[1] *Some Transition-metal Oxalates.*

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Thermodynamic equilibrium constants for the association, in aqueous solution, of nickel, cobalt, and manganese ions with the oxalate ion have been determined by a precise e.m.f. method between 0° and 45°. ΔG, ΔH, and ΔS for the reaction $M^{2+} + C_2O_4^{2-} \rightleftharpoons MC_2O_4$ have been calculated and ΔC_p has been estimated from the variation of ΔH with temperature. The thermodynamic quantities are discussed.

Previous parts of this series have been concerned mainly with ion pairs of only moderate stability. The present work extends the available thermodynamic data to the much more stable oxalate complexes of bivalent transition-metal ions which are known to follow the Irving–Williams order of stability. The identification of complex species present in such solutions is made difficult by the low solubility of the salts. In the presence of an excess of oxalate the solubility increases owing to the formation of increasing amounts of $M(C_2O_4)_2^{2-}$, but we are interested in complexes in which a single anion is associated with each metal ion. Studies of copper oxalate have shown that, with careful control of experimental conditions, supersaturated solutions may be prepared which are stable for long periods.[2] This technique has been extended to cobalt, nickel, and manganese oxalate in the present work, and measurements have been made by using the cell

$$H_2\text{–}Pt|MCl_2,H_2C_2O_4,NaOH|AgCl\text{–}Ag$$

Only in the case of cobalt was it necessary seriously to limit the concentrations to prevent precipitation.

[1] Part VI, Nair and Nancollas, *J.*, 1959, **3934**.
[2] McAuley and Nancollas, *Trans. Faraday Soc.*, 1960, **56**, 1165.

Experimental

Concentrations of stock solutions prepared from "AnalaR" metal chlorides were determined by gravimetric analysis of the chloride as silver chloride; duplicate determinations agreed to within 0·02%. "AnalaR" oxalic acid was recrystallised three times from conductivity water (analysis, 99·9% pure). Hydrochloric acid was constant-boiling material. Carbonate-free sodium hydroxide, prepared from a saturated solution suitably diluted with carbon dioxide-free conductivity water, was standardised both by volume- and by weight-titration against weighed samples of potassium hydrogen phthalate. The apparatus and experimental technique have been described previously.[3] Measurements were made with solutions, stable for at least 24 hr., containing known concentrations of oxalic acid, sodium hydroxide, and the metal chloride. To prevent precipitation, the metal chloride was added slowly only when the other ingredients had been made up nearly to the required volume. E.m.f. readings were constant to within 20 μv.

Results and Discussion

Since only the second thermodynamic dissociation constant of oxalic acid, $K_2 = a_{H^+}a_{C_2O_4^{2-}}/a_{HC_2O_4^-}$, had been determined accurately over a range of temperature,[4] it was necessary to obtain the corresponding values of $K_1 = a_{H^+}a_{HC_2O_4^-}/a_{H_2C_2O_4}$. The first dissociation is rather extensive and measurements were made with a mixed acid cell

$$H_2\text{–}Pt|H_2C_2O_4(m_1),\ HCl(m_4)|AgCl\text{–}Ag$$

the e.m.f. of which is given by

$$E' = E^0 - k \log a_{H^+}a_{Cl^-}$$

or

$$-\log [H^+] = (E' - E^0)/k + \log m_4 + \log \gamma_{H^+}\gamma_{Cl^-}$$

where m represents molality, γ activity coefficient, and $k = 2{\cdot}3026\ \boldsymbol{RT/F}$. By using expressions for total oxalate $m_1 = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]$, electroneutrality

TABLE 1. *Dissociation constant of oxalic acid.*

10^3m_1	10^3m_4	$(E' - E^0)$	$10^3[H^+]$	10^3I	$10^5[C_2O_4^{2-}]$	10^4X	10^5Y
2·9641	2·3993	0·29430	5·1574	5·196	3·842	2·457	1·454
3·8007	2·4028	0·29102	5·9097	5·953	4·362	3·048	1·824
3·6686	4·0032	0·27279	7·3331	7·368	3·466	4·309	2·591
3·5414	4·1377	0·27192	7·3375	7·371	3·329	4·488	2·572
7·6610	5·5797	0·25245	12·1490	12·195	4·553	9·614	5·606
4·7096	4·2582	0·26780	8·4721	8·511	3·899	5·475	3·249
4·2650	4·9781	0·26295	8·7793	8·813	3·416	5·808	3·433
5·0901	4·2715	0·26681	8·8099	8·851	4·068	5·806	3·456
1·9442	1·5601	0·31524	3·4178	3·454	3·658	1·126	0·727

Temp.	0°	15°	25°	35°	45°
10^2k_1	5·70	5·60	5·60	5·18	5·07

$[H^+] = [HC_2O_4^-] + 2[C_2O_4^{2-}] + m_4$, and ionic strength $I = [H^+] + [C_2O_4^{2-}]$, a graphical solution similar to that described by Speakman [5] was applied, leading to an equation

$$Y = XK_1 + K_1K_2$$

in which

$$X = \frac{[H^+]\gamma_2(m_1 - [H^+] - m_4)}{2m_1 - [H^+] + m_4}$$

and

$$Y = \frac{([H^+] - m_4)[H^+]^2\gamma_1^2\gamma_2}{2m_1 - [H^+] + m_4}$$

[3] Nair and Nancollas, *J.*, 1958, 4144.
[4] Robinson and Stokes, "Electrolyte Solutions," Butterworths, London, 1955.
[5] Speakman, *J.*, 1940, 856.

Activity coefficients were obtained from the Davies equation [6]

$$-\log \gamma_z = Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I] \qquad . \; . \; . \; . \; . \quad (1)$$

Fig. 1 shows the good linear relation between X and Y at each temperature. The results at 25° are detailed in Table 1, which includes only the K_1 values at the other temperatures. At 25°, the value agrees very well with $5{\cdot}36 \times 10^{-2}$, obtained from conductivity measurements.[4]

The concentration of hydrogen ions in the cell

$$H_2\text{–}Pt|H_2C_2O_4(m_1),\ NaOH(m_2),\ MCl_2(m_3)|AgCl\text{–}Ag$$

is given by

$$-\log [H^+] = (E' - E^0)/k + \log 2m_3 + \log \gamma_{H^+}\gamma_{Cl^-}$$

The concentrations of ionic species were obtained from: $m_1 = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] + [MC_2O_4]$, $m_3 = [M^{2+}] + [MC_2O_4]$, the electroneutrality condition $[H^+] + 2[M^{2+}] + m_2 = [HC_2O_4^-] + 2[C_2O_4^{2-}] + 2m_3$, and K_1 and K_2 for oxalic acid. Studies on the association between the nickel ion and the malonate and substituted malonate anions both at low concentration and at a number of constant ionic strengths up to $I = 0{\cdot}2$ have

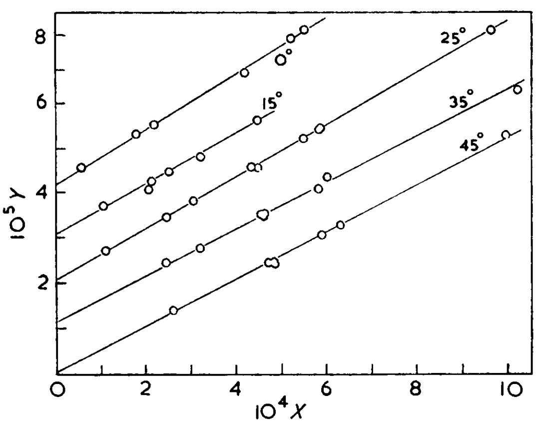

FIG. 1. *Plots of X against Y. (The lines are displaced along the y-axis for clarity.)*

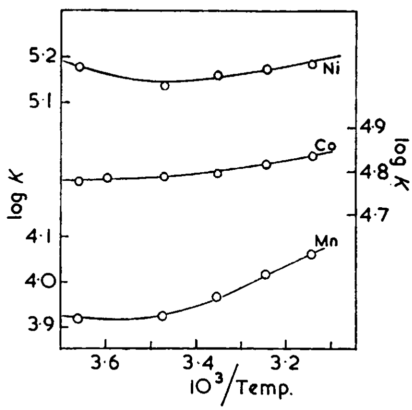

FIG. 2. *Plots of* log K *against* T^{-1}. *(Right-hand ordinates refer to* CoC_2O_4.)

shown that equation (1) represents the activity coefficients very satisfactorily.[7] The same equation has been used in the present work. T.I.P. programmes were constructed for a high-speed DEUCE electronic computer leading to the calculation of thermodynamic association constants $K = \{MC_2O_4\}/\{M^{2+}\}\{C_2O_4^{2-}\}$ by successive approximations of I. Three such approximations were usually carried through, giving 0·1% reproducibility in I. Table 2 shows the good constancy of K at each temperature.

The K values at 25° may be compared with those obtained from conductivity measurements:[8] $K(NiC_2O_4) = 2 \times 10^5$; $K(CoC_2O_4) = 5{\cdot}1 \times 10^4$; and $K(MnC_2O_4) = 8{\cdot}1 \times 10^3$; and, from solubilities, $K(MnC_2O_4) = 9{\cdot}1 \times 10^3$. Plots of log K against T^{-1} in Fig. 2 are curved, indicating a non-zero ΔC_p. This has often been observed in precise measurements on the dissociation of weak acids, but the present is one of the few cases in which detectable values of ΔC_p have been found for reactions involving metal-ion complexes. The variation of log K with temperature may be expressed by the equation $\log K = a + bT + cT^2$, in which the values of the three parameters are as in Table 3. The calculated K values have a maximum difference of 3% from the observed values.

[6] Davies, *J.*, 1938, 2093.
[7] Brannan and Nancollas, unpublished work.
[8] Davies, *Discuss. Faraday Soc.*, 1957, **24**, 83; *J.*, 1938, 2098.

TABLE 2. *E.M.F. measurements.*

Nickel oxalate

Experiment	1	2	3	4	5
10^3m_1	2·9569	3·5174	2·4884	3·2920	1·4138
10^3m_2	0·9450	1·1136	0·8777	1·0339	0·9226
10^3m_3	3·6011	4·3440	3·1053	3·9512	3·1629

Expt.	$(E' - E°)$	10^3I	$10^3[H^+]$	$10^4[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^3[MC_2O_4]$	$10^{-5}K$
			Temp. = 0°				
1	0·25048	9·630	4·0397	8·282	1·914	2·0586	1·53
2	0·24226	11·574	4·8259	9·570	1·913	2·4721	1·62
3	0·25808	8·298	3·3479	6·809	1·851	1·7539	1·46
4	0·24607	10·598	4·4763	9·461	2·006	2·2620	1·52
5	0·27336	8·467	1·7207	1·750	0·929	1·2248	1·43
						Mean $K = 1·51 \pm 0·05$	
			Temp. = 15°				
1	0·26490	9·789	3·9568	9·038	2·014	1·9789	1·36
2	0·25630	11·781	4·7179	10·553	2·041	2·3677	1·42
3	0·27287	8·423	3·2842	7·404	1·936	1·6914	1·32
4	0·26008	10·717	4·4136	10·036	2·038	2·2015	1·44
5	0·28880	8·510	1·6996	1·953	0·988	1·2036	1·33
						Mean $K = 1·37 \pm 0·04$	
			Temp. = 25°				
1	0·27432	9·822	3·9371	9·222	1·919	1·9608	1·42
2	0·26539	11·808	4·7014	10·707	1·932	2·3529	1·50
3	0·28243	8·418	3·2839	7·409	1·798	1·6923	1·44
4	0·26940	10·772	4·3831	10·319	1·962	2·1729	1·47
5	0·29901	8·521	1·6932	2·014	0·950	1·977	1·39
						Mean $K = 1·44 \pm 0·03$	
			Temp. = 35°				
1	0·28403	9·920	3·8795	9·706	1·826	1·9087	1·44
2	0·27470	11·889	4·6499	11·113	1·806	2·3081	1·57
3	0·29240	8·499	3·2369	7·814	1·713	1·6494	1·46
4	0·27884	10·848	4·3349	10·703	1·833	2·1309	1·54
5	0·30941	8·553	1·6756	2·178	0·923	1·1810	1·42
						Mean $K = 1·49 \pm 0·06$	
			Temp. = 45°				
1	0·29365	9·989	3·8401	10·058	1·728	1·8724	1·48
2	0·28406	11·981	4·5978	11·572	1·721	2·2598	1·60
3	0·30227	8·553	3·2060	8·094	1·619	1·6210	1·51
4	0·28829	10·920	4·2933	11·070	1·731	2·0928	1·60
5	0·31977	8·577	1·6627	2·300	0·887	1·1688	1·48
						Mean $K = 1·53 \pm 0·05$	

Cobalt oxalate

Expt.	1	2	3	4	5	6	7	8	9
10^4m_1	10·6015	7·5201	9·9339	4·6320	4·4061	3·3415	4·3336	4·0907	4·4713
10^4m_2	4·3378	4·8485	3·5936	1·9813	2·2535	2·4126	2·5495	1·9679	2·6201
10^4m_3	7·1875	5·7084	5·3596	5·8845	7·5226	8·4511	7·4063	8·0331	9·1779

Expt.	$(E' - E°)$	10^3I	$10^4[H^+]$	$10^4[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^4[MC_2O_4]$	$10^{-4}K$
			Temp. = 0°				
4	0·33709	1·723	5·5981	1·6533	2·222	2·7409	5·60
5	0·33243	2·113	5·3863	1·1516	1·638	3·0803	6·26
6	0·33877	2·367	3·6818	0·5814	1·223	2·6342	5·60
8	0·33164	2·251	5·2324	0·9642	1·420	2·9760	6·20
9	0·32831	2·565	5·3095	0·9954	1·463	3·3207	5·95
						Mean $K = 5·92 \pm 0·26$	
			Temp. = 5°				
4	0·34338	1·723	5·5749	1·6768	2·094	2·7303	5·91
6	0·34513	2·369	3·6613	0·6019	1·178	2·6182	5·78
8	0·33791	2·257	5·1932	1·0031	1·378	2·9412	6·30
9	0·33445	2·567	5·2848	1·0201	1·395	3·3029	6·21
						Mean $K = 6·05 \pm 0·21$	

TABLE 2. (*Continued.*)

Expt.	$(E' - E°)$	10^3I	$10^4[H^+]$	$10^4[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^4[MC_2O_4]$	$10^{-4}K$
			Temp. = 15°				
1	0·33477	2·435	10·8014	5·8534	3·946	4·2483	5·62
2	0·35283	1·848	6·4859	3·6266	3·966	3·4573	5·64
3	0·34364	2·003	10·0386	6·0320	4·293	3·3708	5·84
4	0·35568	1·719	5·5921	1·6593	2·091	2·7479	6·03
5	0·35092	2·119	5·3482	1·1892	1·597	3·0465	6·37
7	0·35302	2·075	4·9883	1·1107	1·596	3·0539	6·54
8	0·34995	2·250	5·2243	0·9722	1·344	2·9756	6·61
9	0·34660	2·572	5·2674	1·0370	1·442	3·2811	5·99
						Mean K = 6·08 ± 0·32	
			Temp. = 25°				
1	0·34646	2·425	10·7932	5·8618	3·659	4·2687	6·18
2	0·36519	1·841	6·4688	3·6436	3·695	3·4674	6·13
3	0·35571	1·999	10·0025	6·0680	4·010	3·3630	6·25
4	0·36843	1·733	5·5157	1·7348	2·051	2·6759	5·89
5	0·36331	2·122	5·3168	1·2202	1·526	3·0224	6·62
7	0·36580	2·095	4·8970	1·2010	1·628	2·9599	6·14
8	0·36267	2·273	5·1204	1·0747	1·405	2·8663	6·02
						Mean K = 6·18 ± 0·15	
			Temp. = 35°				
1	0·35842	2·434	10·6757	5·9676	3·339	4·1892	6·52
2	0·37786	1·847	6·3769	3·7309	3·400	3·4072	6·43
3	0·36801	2·007	9·8810	6·1784	3·663	3·2818	6·47
4	0·38115	1·740	5·4489	1·7992	1·909	2·6246	6·16
5	0·37596	2·136	5·2338	1·3010	1·465	2·9466	6·67
7	0·37842	2·102	4·8415	1·2548	1·525	2·9156	6·44
8	0·37509	2·277	5·0795	1·1142	1·301	2·8365	6·45
9	0·37125	2·586	5·1728	1·1294	1·312	3·2005	6·44
						Mean K = 6·45 ± 0·08	
			Temp. = 45°				
1	0·37024	2·432	10·6254	6·0146	3·041	4·1702	7·14
2	0·39050	1·852	6·3028	3·8033	3·155	3·3585	6·74
3	0·38028	2·015	9·7853	6·2705	3·377	3·2164	6·72
4	0·39386	1·746	5·3926	1·8543	1·788	2·5810	6·43
5	0·38838	2·138	5·2032	1·3309	1·356	2·9272	7·18
7	0·39117	2·113	4·7706	1·3246	1·470	2·8507	6·49
8	0·38762	2·285	5·0261	1·1666	1·239	2·7898	6·65
9	0·38352	2·588	5·1428	1·1588	1·219	3·1801	6·93
						Mean K = 6·79 ± 0·23	

Manganese oxalate

Expt.	1	2	3	4	5	6	7
10^3m_1...	3·4320	4·7888	3·0967	2·6820	6·0543	3·8573	4·5292
10^3m_2...	3·2776	4·4524	2·8542	2·7137	3·1920	5·3869	6·1270
10^3m_3...	9·3107	10·5926	8·9826	7·7665	9·0494	8·6069	8·6630

Expt.	$(E' - E°)$	10^2I	$10^3[H^+]$	$10^3[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^3[MC_2O_4]$	$10^{-3}K$
			Temp. = 0°				
1	0·24805	2·805	1·9402	1·5637	9·437	1·7327	8·37
2	0·23893	3·233	2·5586	2·4025	11·402	2·1902	8·50
3	0·24977	2·705	1·8609	1·4069	8·773	1·5663	8·17
4	0·25855	2·329	1·4553	1·1485	8·830	1·4220	8·01
5	0·22908	2·962	4·5000	3·9386	10·391	1·7728	8·33
						Mean K = 8·28 ± 0·15	
			Temp. = 15°				
1	0·26232	2·811	1·9043	1·5999	9·320	1·6979	8·53
2	0·25270	3·241	2·5125	2·4497	11·229	2·1453	8·69
3	0·26410	2·711	1·8288	1·4391	8·649	1·5354	8·34
4	0·27318	2·331	1·4400	1·1639	8·556	1·4094	8·41
5	0·24208	2·970	4·4585	3·9828	10·052	1·7333	8·64
6	0·28139	2·530	0·9430	1·3499	15·461	2·3354	8·13
7	0·27745	2·574	1·1004	1·7775	17·523	2·5497	8·11
						Mean K = 8·41 ± 0·18	

TABLE 2. (*Continued.*)

Expt.	$(E' - E°)$	10^2I	$10^3[H^+]$	$10^3[HC_2O_4^-]$	$10^5[C_2O_4^{2-}]$	$10^3[MC_2O_4]$	$10^{-4}K$
			Temp. = 25°				
1	0·27154	2·808	1·9060	1·5986	8·672	1·7058	0·941
2	0·26152	3·237	2·5218	2·4413	10·396	2·1625	0·969
3	0·27321	2·706	1·8423	1·4261	7·927	1·5559	0·943
4	0·28282	2·329	1·4384	1·1658	7·991	1·4133	0·921
5	0·25066	2·969	4·4532	3·9904	9·402	1·7334	0·944
6	0·29138	2·527	0·9396	1·3536	14·500	2·3415	0·889
7	0·28727	2·570	1·0978	1·7805	16·390	2·5583	0·889
					Mean K = 0·928 ± 0·024		
			Temp. = 35°				
1	0·28101	2·808	1·8905	1·6105	7·864	1·7002	1·06
2	0·27065	3·236	2·5025	2·4539	9·407	2·1565	1·09
3	0·28270	2·705	1·8296	1·4357	7·172	1·5524	1·06
4	0·29271	2·329	1·4240	1·1781	7·276	1·4071	1·03
5	0·25940	2·968	4·4221	4·0024	8·481	1·7210	1·06
6	0·30162	2·524	0·9280	1·3638	13·192	2·3436	1·00
7	0·29735	2·566	1·0852	1·7910	14·879	2·5618	1·00
					Mean K = 1·04 ± 0·03		
			Temp. = 45°				
1	0·29055	2·809	1·8735	1·6268	7·271	1·6894	1·16
2	0·27986	3·237	2·4803	2·4749	8·690	2·1420	1·20
3	0·29222	2·705	1·8179	1·4468	6·596	1·5467	1·18
4	0·30261	2·329	1·4112	1·1905	6·723	1·4000	1·13
5	0·26817	2·971	4·3939	4·0271	7·793	1·7015	1·17
6	0·31194	2·522	0·9157	1·3760	12·226	2·3410	1·10
7	0·30741	2·564	1·0736	1·8024	13·719	2·5619	1·11
					Mean K = 1·15 ± 0·03		

ΔH, ΔC_p, and ΔS calculated from the equations $\Delta H = 2{\cdot}303\boldsymbol{R}T^2(b + 2cT)$, $\Delta C_p = 4{\cdot}606\boldsymbol{R}T(b + 3cT)$, and $\Delta S = (\Delta H - \Delta G)/T$, are given in Table 4. The mean deviations have been estimated by using different combinations of experimental points at three temperatures for the calculation of a, b, and c.

The values of ΔC_p may be compared with 35—45 cal. deg.$^{-1}$ for a number of reactions in which hydrogen ion associates with an anion.[9] $\Delta C_p(CoC_2O_4)$ appears to be rather low, but the larger values for NiC_2O_4 and MnC_2O_4 reflect the trend with charge type observed in proton-transfer reactions. A ΔC_p of 70 cal. deg.$^{-1}$ has been found for the association of tervalent chromium with thiocyanate ion.[10]

The entropy of association may be written:

$$\Delta S = \Delta S_g + \Delta S_{hyd}(MC_2O_4) - \Delta S_{hyd}(M^{2+}) - \Delta S_{hyd}(C_2O_4^{2-}) \quad . \quad . \quad (2)$$

where ΔS_g and ΔS_{hyd} are respectively gaseous and hydration entropies. ΔS_g has been calculated as described previously,[11] by using a non-planar model for the complex species with the M–O and oxalate planes at an angle of 101°. $\Delta S_{hyd}(MC_2O_4)$ obtained from equation (2) is given in Table 5. The values are lower than the 63—71 cal. deg.$^{-1}$ mole^{-1} observed for the corresponding sulphate ion pairs; this may be due to a greater neutralisation of charge accompanying the formation of oxalate complexes. The change in $\Delta S_{hyd}(MC_2O_4)$ is small but, as far as differences are significant, it varies in the expected

TABLE 3. *Parameters for temperature-dependence of* log K.

	a	-10^2b	10^5c
NiC_2O_4	9·065	2·655	4·512
CoC_2O_4	6·810	1·500	2·760
MnC_2O_4	8·141	3·146	5·857

The calculated K values have a maximum difference of 3% from the observed values.

[9] Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.
[10] Postmus and King, *J. Phys. Chem.*, 1955, **59**, 1208.
[11] Nair and Nancollas, *J.*, 1958, 3706.

direction with the reciprocal of the cationic radius. The entropy of association increases with temperature and the values at 0° and 45° are respectively; NiC_2O_4, 21·0 and 28·2; CoC_2O_4, 22·0 and 25·8; MnC_2O_4, 18·6 and 27·0 cal. deg.$^{-1}$ mole^{-1}. This increase reflects the greater freedom of the "frozen" solvent molecules when released from the fields of the ions at the higher temperatures.

TABLE 4. *Thermodynamic properties*

Reaction	ΔH (kcal. mole^{-1})	ΔG_{298} (kcal. mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	ΔC_p (cal. deg.$^{-1}$)
$Ni^{2+} + C_2O_4^{2-}$	0·15 ± 0·10	−7·05 ± 0·02	24·2 ± 0·4	35 ± 12
$Co^{2+} + C_2O_4^{2-}$	0·59 ± 0·07	−6·54 ± 0·02	23·9 ± 0·3	20 ± 10
$Mn^{2+} + C_2O_4^{2-}$	1·42 ± 0·20	−5·41 ± 0·02	22·9 ± 0·7	65 ± 15

TABLE 5. *Thermodynamic properties*

Ion pair	$S_g(MC_2O_4)$ (cal. deg.$^{-1}$ mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	$S°(MC_2O_4)$ (cal. deg.$^{-1}$ mole^{-1})	$-\Delta S_{hyd}(MC_2O_4)$ (cal. deg.$^{-1}$ mole^{-1})	r_+^{-1} (Å^{-1})
NiC_2O_4	70·0	24·7	13·9	56·1	1·37
CoC_2O_4	70·0	23·9	14·1	55·8	1·35
MnC_2O_4	69·9	22·9	15·1	54·8	1·28

The heat changes, ΔH, oppose the association reactions and it is these terms which account for the considerable differences of stability over the series of cations. This is to be expected for transition-metal ion complexes, and it has also been claimed that equations of the form

$$\Delta H = Az/r_+ + BI_{02} - C/r_+^3$$

may be used to represent the data.[12] The ΔH values of Table 4 follow the reverse of this order, decreasing with increasing r_+^{-1} and ionization potential I_{02}. When ΔH is expressed by an equation analogous to (2), and all other terms are assumed to be approximately constant, ΔH should increase with $-\Delta H_{hyd}(M^{2+})$; the opposite order is observed: more results are required to explain this.

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[12] Williams, *J. Phys. Chem.*, 1954, **58**, 121.