878. *Thermodynamics of Ion Association. Part IX.*[1] *Some Transition-metal Succinates.*

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E.m.f.s of cells of the type H_2, Pt|H_2A, NaOH, MCl_2|AgCl/Ag, where H_2A represents succinic acid, measured by a precision method at temperatures from 0° to 45°, are interpreted in terms of the formation of NiA, CoA, and MnA, and the corresponding hydrogen succinates, $NiHA^+$ and $MnHA^+$. Preliminary pH measurements, in which a glass electrode was used, at a constant ionic strength (0·2M) were used to identify the ion-pairs present in the solutions. ΔH, ΔG, ΔS, and ΔC_p are evaluated for the reaction $M^{2+} + A^{2-} \rightleftharpoons MA$, and these are discussed.

Of the transition-metal dicarboxylates, the ion-pairs formed with the succinate ion involve the much less stable seven-membered ring. The smaller difference between the dissociation constants of succinic acid than between those of oxalic [2] or malonic acid [1] increases the concentration of HA^- ions, and ion-pairs such as MHA^+ have to be taken into account as well as MA when considering cells such as H_2, Pt|H_2A, NaOH, MCl_2|AgCl/Ag.

Experimental

"AnalaR" salts were used where available. Sodium perchlorate solutions were prepared from the recrystallised material and analysed by using an Amberlite IR-120 ion-exchange resin (H^+ form).

pH measurements at constant ionic strength, both in the acid buffer and in the presence of manganese ions, were made with a glass electrode in a cell of the type

Ag/AgCl, HCl|glass|solution under study|sat. KCl|calomel electrode

Glass electrodes were either commercial screened electrodes (E.I.L. type GG33), or were made from Corning 015 glass. The cell, incorporating Dunsmore and Speakman's [3] reproducible liquid junction, was maintained at 25° in an oil-bath even when not in use to prevent fluctuating calomel electrode potentials. E.M.F. measurements were made with a Tinsley potentiometer and Vibron electrometer (E.I.L. model 33B) as a null indicator; readings were reproducible to ±0·1 mv. Electrode systems were standardised with 0·01M-hydrochloric acid + 0·09M-potassium chloride which has a pH of 2·078,[4] and with 0·05M-potassium hydrogen phthalate (pH = 4·005 [5]); $[H^+]$ was obtained from pH ($= -\log a_{H^+}$) by using the mean activity data for hydrochloric acid given by Robinson and Stokes.[6] The procedure consisted in determining the pH of solutions containing known concentrations of succinic acid, sodium hydroxide, and manganese chloride, with sufficient sodium perchlorate to maintain an ionic strength of 0·2M.

For e.m.f. measurements with the cell

(1) H_2, Pt|$H_2A(m_1)$, NaOH(m_2), $MCl_2(m_3)$|AgCl/Ag

The apparatus, standardisation of electrodes, and experimental technique have been described previously.[7]

Results and Discussion

E.m.f.s of cells (1) could not be interpreted in terms of only one complex MA and, in order to identify the other species present, pH measurements were made in solutions of constant ionic strength 0·2M.

It was first necessary to obtain the dissociation constants, $k_1{}^1 = [H^+][HA^-]/[H_2A]$ and

[1] Part VIII, *J.*, 1961, 4367.
[2] McAuley and Nancollas, *J.*, 1961, 2215.
[3] Dunsmore and Speakman, *Trans. Faraday Soc.*, 1954, **50**, 236.
[4] Hitchcock and Taylor, *J. Amer. Chem. Soc.*, 1938, **60**, 2710.
[5] British Standard, 1647, 1950.
[6] Robinson and Stokes, "Electrolyte Solutions," Butterworths, London, 1955.
[7] Nair and Nancollas, *J.*, 1958, 4144.

$k_2^1 = [H^+][A^{2-}]/[HA^-]$, of succinic acid at this ionic strength, and pH measurements were made in mixtures of succinic acid, sodium hydroxide, and sodium perchlorate. A graphical solution similar to that described by Speakman [8] was applied, leading to an equation $X = k_1^1Y + k_1^1k_2^1$, where

$$X = [H^+]^2\{[HA^-] + 2[A^{2-}]\}/\{2[H_2A] + [HA^-]\}$$

and

$$Y = [H^+]\{[H_2A] - [A^{2-}]\}/\{2[H_2A] + [HA^-]\}.$$

The results are summarised in Table 1 and X is plotted against Y in Fig. 1; the slope and intercept give $k_1^1 = 1{\cdot}38 \times 10^{-4}$ and $k_2^1 = 6{\cdot}9 \times 10^{-6}$.

In the concentration ranges used in this work, the complex species expected in solutions containing metal chloride, succinic acid, and sodium hydroxide are MA and MHA^+. A comprehensive treatment at low concentration would involve equations for total metal-ion concentration $m_3 = [M^{2+}] + [MHA^+] + [MA]$, for total succinic acid concentration $m_1 = [H_2A] + [HA^-] + [A^{2-}] + [MA] + [MHA^+]$, for electroneutrality $m_2 + [H^+] + 2[M^{2+}] + [MHA^+] = [HA^-] + 2[A^{2-}] + 2m_3$, and for the thermodynamic dissociation constants of succinic acid $k_1 = [H^+][HA^-]\gamma_1^2/[H_2A]$ and $k_2 = [H^+][A^{2-}]\gamma_2/[HA^-]$. The required association constants are $K = [MA]/[M^{2+}][A^{2-}]\gamma_2^2$, $K_1 = [MHA^+]/[M^{2+}][HA^-]\gamma_2$, and $I = 3m_3 - m_1 + 4[A^{2-}] + [H_2A] + 2[HA^-]$.

TABLE 1.

Dissociation constants of succinic acid at 25°, $I = 0{\cdot}2$M.

10^3T_A *	$10^3[Na^+]$	$10^4[H^+]$	10^4X	10^8Y	10^3T_A *	$10^3[Na^+]$	$10^4[H^+]$	10^4X	10^8Y
7·099	2·192	2·647	1·05	1·47	7·099	3·245	1·602	0·55	0·81
7·099	2·543	2·271	0·86	1·25	12·660	7·084	1·156	0·35	0·53
7·099	2·456	2·295	0·88	1·23	12·660	14·722	0·181	−0·036	0·045
7·099	2·731	2·064	0·76	1·11	12·660	20·543	0·0437	−0·072	0·008

* T_A = Total succinic acid concentration.

At constant ionic strength, activity coefficients are omitted and the corresponding stability constants are written K^1 and K_1^1. pH measurements were made with manganese succinate over a range of concentration of metal ion and are summarised in Table 2.

TABLE 2.

Manganese succinate at 25°, $I = 0{\cdot}2$M ($K_1^1 = 5$ l. mole^{-1}).

$10^4[H^+]$	10^3m_3	10^3m_1	$10^3[Na^+]$	$10^3[HA^-]$	$10^3[A^{2-}]$	$10^3[MA]$	$10^3[MHA^+]$	K_1^1	K^1
1·308	18·310	12·660	7·084	5·711	0·330	0·154	0·536	5·3	26·5
0·2079	7·324	12·660	14·772	7·744	2·809	0·552	0·277	5·5	30·3
0·2414	18·310	12·660	14·772	7·215	2·254	1·214	0·595	5·0	32·6
0·2740	36·620	12·660	14·772	6·566	1·807	1·710	1·149	5·2	28·0
0·0566	18·310	12·660	20·543	4·076	5·430	2·642	0·329	5·3	31·7
0·06528	36·620	12·660	20·790	3·562	4·114	4·208	0·591	5·2	32·1

Mean $K_1^1 = 5{\cdot}1$. Mean $K^1 = 30{\cdot}1$.

Various values of K_1^1 were inserted and a constant K^1 was obtained over a 23-fold variation in $[H^+]$ with $K_1^1 = 5$ l. mole^{-1} at $I = 0{\cdot}2$M. This provides confirmatory evidence that the second complex present in these solutions is MHA^+.

Precise e.m.f. measurements at low concentrations were then made at each temperature and K was calculated, by means of a DEUCE electronic computer, for various values of K_1 by successive approximations of I with the activity coefficient expression [9] $-\log \gamma_z = Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I]$ and the thermodynamic dissociation constants of succinic acid determined by Pinching and Bates.[10] K values at each chosen K_1 between 0 and 40 l.

[8] Speakman, *J.*, 1940, 855.
[9] Davies, *J.*, 1938, 2093.
[10] Pinching and Bates, *J. Res. nat. Bur. Stand.*, 1950, **45**, 322, 444.

mole^{-1} are given in Table 3. The mean deviation in K passes through a minimum and the corresponding K_1 was taken as the correct value; for Ni^{2+}, $K_1 = 20$; for Mn^{2+}, $K_1 = 15$; and for Co^{2+}, $K_1 = 0$. Calculation showed that these were also the best values at

TABLE 3.

Association constants at 25°.

	Nickel		Cobalt		Manganese	
K_1	$10^{-2}K$	Dev. in K (%)	$10^{-2}K$	Dev. in K (%)	$10^{-2}K$	Dev. in K (%)
0	2·13	12·5	1·65 *	3·6	1·79	15·6
2	—	—	1·67	4·5	—	—
5	2·15	9·6	1·72	5·4	1·80	10·0
10	2·17	6·6	1·79	6·6	1·82	4·7
15	2·19	3·9	1·85	8·8	1·84 *	2·2
20	2·21 *	2·3	1·92	10·5	1·86	5·5
25	2·23	2·7	1·99	12·1	1·87	10·8
30	2·25	5·3	—	—	—	—
40	2·29	10·4	—	—	—	—

* K and K_1 values adopted at 25°.

the other temperatures. The cobalt experiments were designed to limit the effect of MHA^+ and it is seen that a zero concentration of this species gives the best constancy of K. By using the appropriate K_1 values, K was evaluated at each temperature and

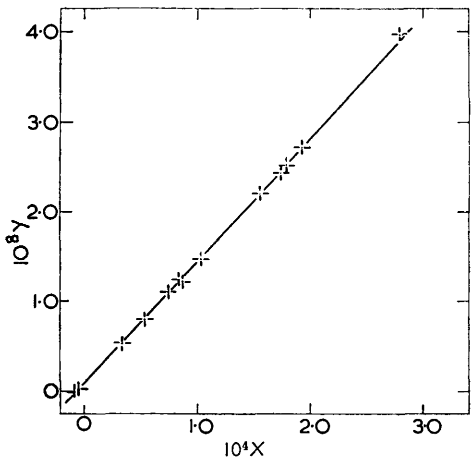

FIG. 1. Plots of X against Y.

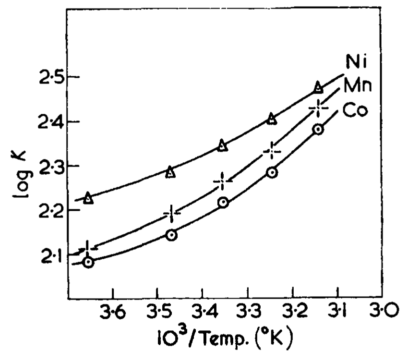

FIG. 2. Plots of log K against T^{-1}.

Table 4 shows the very good constancy obtained. The values at 25° may be compared with those given by Davies;[11] $K(CoA) = 2{\cdot}7 \times 10^2$, $K(NiA) = 2{\cdot}46 \times 10^2$, and $K(MnA) = 1{\cdot}78 \times 10^2$. The agreement is very good except in the case of cobalt.

By using γ_1 and γ_2 at $I = 0{\cdot}2$ estimated from the activity coefficient expression, K^1 values for manganese succinate, reduced to $I \longrightarrow 0$, become $K = 200$ and $K_1 = 13$, in excellent agreement with 184 and 15, respectively, in Tables 3 and 4.

Plots of log K against T^{-1} in Fig. 2 show marked curvature and may be expressed, with an accuracy of 3% in K, by the equation $\log K = a + bT + cT^2$. Values of the parameters, evaluated as described previously,[2] are given in Table 5. ΔG, ΔH, ΔC_p, and ΔS calculated from the equations $\Delta G = -\boldsymbol{R}T \ln K$, $\Delta H = 2{\cdot}303\boldsymbol{R}T^2(b + 2cT)$, $\Delta C_p = 4{\cdot}606\boldsymbol{R}T(b + 3cT)$, and $\Delta S = (\Delta H - \Delta G)/T$, are given in Table 6. ΔC_p is again seen to be subject to the greatest uncertainty. $-\Delta G$ is considerably smaller than for the

[11] Davies, *Discuss. Faraday Soc.*, 1957, **24**, 83.

TABLE 4.

Nickel succinate (K_1 = 20 l. mole^{-1}).

Expt.	1	2	3	4	5	6	7	8
10^3m_1 ...	2·64432	2·89030	2·61753	2·86422	5·21511	6·24147	9·15003	11·7692
10^3m_2 ...	3·48105	4·24597	2·22955	3·20346	7·99195	6·25450	8·58724	9·92814
10^3m_3 ...	3·97073	3·95576	5·08036	4·26079	7·24212	4·26849	5·61057	10·62220

Expt.	$E^1 - E°$	10^6[H⁺]	10^2I	10^3[HA⁻]	10^4[A²⁻]	10^3[M²⁺]	10^4[MA]	$10^{-2}K$
				At 0°				
1	0·40142	6·361	1·548	1·458	7·863	3·712	1·954	1·76
2	0·41305	3·874	1·642	1·319	11·824	3·643	2·539	1·59
6	0·37687	16·960	1·899	4·014	8·482	3·896	1·855	1·64
7	0·36519	21·889	2·503	5·759	10·055	5·031	2·591	1·67
8	0·34184	33·181	4·038	6·832	8·913	9·628	3·519	1·71
							Mean	1·67 ± 0·05
				At 15°				
3	0·37908	29·899	1·732	1·616	2·072	4·918	0·674	1·87
4	0·40359	13·155	1·589	1·799	5·146	4·022	1·507	1·98
5	0·42051	4·211	2·938	2·080	21·512	6·366	7·376	1·96
6	0·39479	19·079	1·893	4·032	8·267	3·883	2·030	1·86
7	0·38238	24·730	2·495	5·782	9·767	5·014	2·798	1·91
8	0·35768	37·645	4·031	6·859	8·649	9·617	3·716	1·93
							Mean	1·92 ± 0·04
		10^5[H⁺]						
				At 25°				
1	0·43442	0·737	1·538	1·648	0·758	3·689	2·202	2·15
3	0·39088	3·157	1·729	1·617	1·999	4·912	0·752	2·20
4	0·41660	1·373	1·585	1·805	5·030	4·014	1·595	2·18
5	0·43388	0·444	2·910	2·083	20·800	6·297	8·085	2·28
6	0·40734	2·004	1·885	4·043	8·028	3·865	2·226	2·15
7	0·39441	2·608	2·484	5·794	9·447	4·989	3·088	2·24
8	0·36873	3·994	4·019	6·861	8·322	9·589	4·087	2·27
							Mean	2·21 ± 0·05
				At 35°				
1	0·44860	0·751	1·530	1·472	7·366	3·670	2·395	2·46
3	0·40334	3·260	1·726	1·621	1·919	4·905	0·821	2·55
4	0·43000	1·408	1·579	1·811	4·863	4·001	1·737	2·51
5	0·44801	0·453	2·888	2·088	20·221	6·243	8·649	2·59
6	0·42043	2·056	1·877	4·060	7·767	3·848	2·413	2·46
7	0·40698	2·685	2·474	5·816	9·117	4·969	3·324	2·56
8	0·38029	4·141	4·008	6·877	7·982	9·565	4·397	2·62
							Mean	2·53 ± 0·05
				At 45°				
1	0·46313	0·749	1·522	1·478	7·134	3·650	2·603	2·82
3	0·41617	3·304	1·723	1·625	1·830	4·899	0·895	2·98
4	0·44374	1·426	1·571	1·814	4·633	3·980	1·956	3·03
5	0·46249	0·456	2·856	2·093	19·389	6·164	9·471	3·05
6	0·43403	2·069	1·868	4·078	7·469	3·828	2·632	2·85
7	0·42011	2·708	2·464	5·842	8·761	4·947	3·569	2·93
8	0·39235	4·212	3·996	6·892	7·608	9·540	4·737	3·04
							Mean	2·96 ± 0·08

Cobalt succinate (K_1 = 0)

Expt.	1	2	3	4	5	6
10^3m_1	4·5096	5·0085	3·6668	3·7054	3·8596	3·7091
10^3m_2	4·5314	4·8902	5·1766	5·1137	5·0583	4·7523
10^3m_3	6·5698	7·0268	5·4807	5·8234	5·9076	5·5273

Expt.	$E^1 - E°$	10^5[H⁺]	10^2I	10^3[HA⁻]	10^3[A²⁻]	10^4[MA]	$10^{-2}K$
			At 0°				
1	0·36658	1·757	2·446	2·971	0·643	1·465	1·15
2	0·36272	1·952	2·615	3·282	0·650	1·640	1·23
3	0·39994	0·505	2·219	1·877	1·381	2·711	1·16
4	0·39579	0·569	2·304	1·968	1·296	2·803	1·23
5	0·39025	0·710	2·314	2·202	1·163	2·688	1·29
6	0·39012	0·757	2·172	2·178	1·063	2·285	1·24
						Mean	1·24 ± 0·04

TABLE 4. (*Continued.*)

Expt.	$E^1 - E^\circ$	$10^5[H^+]$	10^2I	$10^3[HA^-]$	$10^3[A^{2-}]$	$10^4[MA]$	$10^{-2}K$
			At 15°				
3	0·41944	0·561	2·212	1·883	1·362	2·880	1·29
4	0·41502	0·634	2·297	1·974	1·276	2·977	1·36
5	0·40924	0·789	2·310	2·211	1·149	2·782	1·39
6	0·40877	0·852	2·161	2·182	1·033	2·562	1·47
						Mean	1·37 ± 0·05
			At 25°				
1	0·39599	2·089	2·433	2·986	0·605	1·787	1·56
2	0·39183	2·316	2·603	3·302	0·614	1·918	1·60
3	0·43279	0·590	2·194	1·884	1·316	3·331	1·58
4	0·42809	0·670	2·278	1·974	1·226	3·472	1·69
5	0·42203	0·837	2·291	2·210	1·101	3·274	1·75
6	0·42192	0·891	2·151	2·187	1·007	2·799	1·69
						Mean	1·65 ± 0·06
			At 35°				
1	0·40864	2·150	2·426	2·995	0·584	1·954	1·81
2	0·40426	2·391	2·595	3·310	0·590	2·121	1·88
3	0·44678	0·604	2·177	1·887	1·273	3·752	1·89
4	0·44201	0·684	2·264	1·978	1·191	3·806	1·96
5	0·43564	0·858	2·277	2·215	1·064	3·616	2·05
6	0·43547	0·916	2·137	2·191	0·972	3·140	2·01
						Mean	1·93 ± 0·07
			At 45°				
1	0·42137	2·202	2·411	2·990	0·548	2·338	2·37
2	0·41700	2·436	2·582	3·310	2·559	2·437	2·35
3	0·46114	0·610	2·154	1·889	1·215	4·321	2·34
4	0·45608	0·694	2·240	1·979	1·130	4·405	2·45
5	0·44959	0·868	2·257	2·217	1·015	4·102	2·50
6	0·44945	0·925	2·120	2·194	0·928	3·562	2·45
						Mean	2·41 ± 0·06

Manganese succinate ($K_1 = 15$)

Expt.	1	2	3	4	5	6	7	8
10^3m_1 ...	3·87732	3·58060	4·10579	3·73456	3·84355	3·70642	7·12848	8·07886
10^3m_2 ...	2·72403	3·64612	3·40891	3·65978	4·42001	4·20629	8·56922	9·41907
10^3m_3 ...	4·89358	5·65596	4·90255	3·54878	9·83515	8·44751	10·28948	9·68893

Expt.	$E^1 - E^\circ$	$10^5[H^+]$	10^2I	$10^3[HA^-]$	$10^4[A^{2-}]$	$10^3[M^{2+}]$	$10^4[MA]$	$10^{-2}K$
				At 0°				
1	0·35267	4·096	1·731	2·201	1·888	4·753	0·458	1·41
2	0·37151	1·620	2·060	2·290	5·182	5·438	1·092	1·16
3	0·36168	2·822	1·802	2·537	3·186	4·718	0·777	1·45
5	0·36559	1·274	3·359	2·285	7·386	9·417	2·523	1·38
7	0·36851	1·098	3·915	4·151	16·220	9·550	4·460	1·19
8	0·36778	1·200	3·832	4·833	17·188	8·948	4·194	1·11
							Mean	1·28 ± 0·13
				At 15°				
1	0·36921	4·617	1·730	2·213	1·838	4·752	0·476	1·54
5	0·38291	1·437	3·353	2·293	7·201	9·403	2·686	1·55
6	0·38621	1·436	2·927	2·253	6·825	8·075	2·297	1·52
7	0·38543	1·264	3·882	4·148	15·407	9·470	5·332	1·55
8	0·38453	1·388	3·791	4·822	16·211	8·848	5·278	1·54
							Mean	1·54 ± 0·02
				At 25°				
1	0·38077	4·869	1·729	2·218	1·777	4·747	0·532	1·81
5	0·39468	1·531	3·340	2·292	6·884	9·371	3·029	1·88
6	0·39818	1·527	2·916	2·252	6·539	8·046	2·602	1·83
7	0·39730	1·348	3·854	4·145	14·718	9·402	6·065	1·90
8	0·39666	1·463	3·773	4·832	15·708	8·804	5·759	1·78
							Mean	1·84 ± 0·04
				At 35°				
3	0·40296	3·435	1·795	2·570	2·913	4·705	0·926	2·01
4	0·42438	2·066	1·424	2·471	4·422	3·349	1·246	2·26
5	0·40702	1·592	3·327	2·293	6·566	9·341	3·356	2·23
6	0·41074	1·581	2·905	2·255	6·264	8·021	2·872	2·16
7	0·41010	1·383	3·839	4·161	14·286	9·368	6·434	2·13
8	0·40925	1·511	3·751	4·843	15·109	8·752	6·326	2·09
							Mean	2·15 ± 0·07

TABLE 4. (*Continued.*)

Expt.	E^1-E°	$10^5[H^+]$	10^2I	$10^3[HA^-]$	$10^4[A^{2-}]$	$10^3[M^{2+}]$	$10^4[MA]$	$10^{-2}K$
				At 45°				
4	0·43792	2·093	1·417	2·476	4·211	3·330	1·439	2·80
5	0·41962	1·637	3·310	2·289	6·154	9·299	3·800	2·78
6	0·42334	1·633	2·887	2·249	5·836	7·976	3·347	2·78
7	0·42309	1·407	3·812	4·167	13·572	9·302	7·147	2·57
8	0·42212	1·543	3·719	4·846	14·298	8·675	7·154	2·58
							Mean	2·70 ± 0·10

TABLE 5.

Parameters for temperature-dependence of log K.

	a	-10^2b	10^5c
NiA	3·560	1·384	3·274
CoA	6·041	3·255	6·615
MnA	4·006	1·912	4·453

corresponding malonate complexes [1] owing to the lower stability of the seven-membered ring.

$\Delta S_{hyd}(MA)$ may be written:

$$\Delta S_{hyd}(MA) = \Delta S - \Delta S_g + \Delta S_{hyd}(M^{2+}) + \Delta S_{hyd}(A^{2-})$$

where ΔS_{hyd} and ΔS_g are hydration and gaseous entropies respectively. ΔS_g has been calculated as described previously,[12] a planar model being used for the complex species.

TABLE 6.

Thermodynamic properties.

Reaction	ΔH (kcal. mole^{-1})	ΔG (kcal. mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	ΔC_p (cal. deg.$^{-1}$)
$Ni^{2+} + A^{2-}$	2·23 ± 0·2	−3·20 ± 0·02	18·2 ± 0·7	42 ± 20
$Co^{2+} + A^{2-}$	2·81 ± 0·04	−3·02 ± 0·02	19·6 ± 0·1	72 ± 20
$Mn^{2+} + A^{2-}$	2·95 ± 0·1	−3·09 ± 0·02	20·3 ± 0·2	62 ± 15

TABLE 7.

Entropies (in cal. deg.$^{-1}$ mole^{-1}).

Ion pair	$S_g(MA)$	ΔS	$S^\circ(MA)$	$-\Delta S_{hyd}(MA)$	r_+^{-1} (Å^{-1})
NiA	70·6	18·2	+1·1	69·5	1·37
CoA	70·6	19·6	+3·5	67·1	1·35
MnA	70·5	20·3	+6·2	64·4	1·28

$\Delta S_{hyd}(A^{2-})$ was interpolated on a plot of ΔS_{hyd} of a number of bivalent anions against r_-^{-1}, r_- having been calculated from the corresponding ionic mobilities.[13] Entropies are summarised in Table 7. $\Delta S_{hyd}(MA)$ follow the order oxalate > malonate > succinate and may reflect an increasing polarity of the complexes accompanying reduced stability. The importance of using hydration entropies, and not entropies of association for correlation with r_+^{-1}, is seen in Table 7; the two terms vary in opposite directions.

Heats of formation vary in the same sense as for the oxalates and malonates, in the reverse order to changes in ionisation potential I_{02}.

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