860. *Thermodynamics of Ion Association. Part VIII.*[1] *Some Transition-metal Malonates.*

By V. S. K. Nair and G. H. Nancollas.

Thermodynamic equilibrium constants for the association in aqueous solution of nickel, cobalt, and manganese ions with the malonate ion have been determined at various temperatures between 0° and 45° from the e.m.f.s of cells $H_2,Pt|H_2Mal,NaOH,MCl_2|AgCl/Ag$ (Mal = malonate). ΔG, ΔH, ΔS, and ΔC_p are evaluated for the reaction $M^{2+} + Mal^{2-} \rightleftharpoons MMal$, and these are discussed.

Part VII of this series [1] was concerned with the study of the stable five-membered ring chelate compounds formed between nickel, cobalt, and manganese ions and oxalate ion. The investigation has now been extended to the malonate complexes which contain less stable six-membered rings. The malonates do not suffer from the disadvantage of very low solubilities, and it has been possible to make measurements over a wider concentration range than with the oxalates, by using the cell:

$$H_2Pt|H_2Mal(m_1),NaOH(m_2),MCl_2(m_3)|AgCl/Ag \quad (1)$$

Experimental

"AnalaR" salts were used where available and solutions were made up by weight with conductivity water. Malonic acid was recrystallised from 1 : 1 ether–benzene containing 5% of light petroleum (b. p. 60—80°) and was dried *in vacuo* at 40—50° (Found: H, 4·0; C, 34·8. Calc. for $C_3H_4O_4$: H, 3·9; C, 34·6%). The e.m.f. apparatus and experimental procedure have been described previously.[1,2]

Results and Discussion

It was necessary to determine the primary dissociation constant of malonic acid at the temperatures to be used. Measurements were made with the cell

$$H_2Pt|H_2Mal(m_1),KCl(m_4)|AgCl/Ag$$

for which

$$-\log [H^+] = (E - E^\circ)/k + \log m_4 + \log \gamma_1^2,$$

where m represents molality, γ activity coefficient, and $k = 2{\cdot}3026\ \boldsymbol{RT/F}$. The concentrations of ionic species were obtained from equations for total malonate $m_1 = [H_2Mal] + [HMal^-] + [Mal^{2-}]$, electroneutrality $[H^+] = [HMal^-] + 2[Mal^{2-}]$, the second dissociation

[1] Part VII, McAuley and Nancollas, *J.*, 1961, 2215.
[2] Nair and Nancollas, *J.*, 1958, 4144.

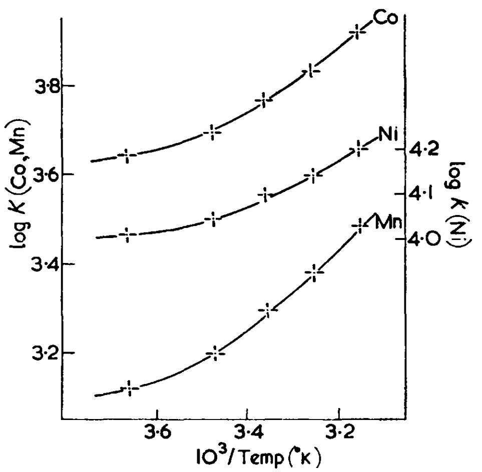
constant[3] $k_2 = [H^+][Mal^{2-}]\gamma_2/[HMal^-]$, and ionic strength $I = [H^+] + [Mal^{2-}] + m_4$. k_1 $(=[H^+][HMal^-]\gamma_1{}^2/[H_2Mal])$ was calculated by successive approximation of I with use of the activity coefficient expression[4] $-\log\gamma_z = Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I]$, and the results are given in Table 1. k_1 at 25° agrees well with $1{\cdot}4 \times 10^{-3}$ obtained by Jeffrey and Vogel from conductivity measurements.[5]

TABLE 1.

Primary dissociation constant of malonic acid.

Experiment	1	2	3	4
10^3m_1	2·6185	5·1880	7·3493	10·5587
10^3m_4	7·8490	9·5991	8·9302	9·0812

Temp.	Expt.	$(E - E^\circ)/k$	$10^3[H^+]$	10^3I	$10^3[HMal^-]$	10^3k_1
0°	1	5·0460	1·390	9·242	1·384	1·29
	2	4·7709	2·189	11·79	2·183	1·28
	3	4·7061	2·743	11·68	2·736	1·31
	4	4·6069	3·394	12·48	3·388	1·29
					Mean	1·29
15	1	5·0377	1·424	9·276	1·418	1·38
	2	4·7608	2·253	11·86	2·247	1·38
	3	4·6952	2·814	11·75	2·808	1·40
	4	4·5964	3·499	12·58	3·492	1·38
					Mean	1·38
25	1	5·0345	1·440	9·292	1·434	1·43
	2	4·7571	2·282	11·88	2·276	1·43
	3	4·6913	2·853	11·786	2·846	1·44
	4	4·5921	3·548	12·63	3·542	1·42
					Mean	1·43
35	1	5·0356	1·442	9·294	1·436	1·43
	2	4·7578	2·288	11·89	2·283	1·43
	3	4·6921	2·859	11·79	2·853	1·44
	4	4·5925	3·562	12·64	3·556	1·43
					Mean	1·43
45	1	5·0402	1·433	9·285	1·428	1·40
	2	4·7621	2·277	11·88	2·271	1·40
	3	4·6960	2·847	11·78	2·842	1·42
	4	4·5957	3·552	12·63	3·546	1·41
					Mean	1·41



Plots of K against T^{-1}. (Right-hand ordinates refer to Ni.)

E.m.f.s of cell (1) were measured over a range of concentration, and the thermodynamic association constants $K = \{MMal\}/\{M^{2+}\}\{Mal^{2-}\}$ were calculated as described in Part VII.

[3] Hamer, Burton, and Acree, *J. Res. Nat. Bur. Stand.*, 1940, **24**, 292.
[4] Davies, *J.*, 1938, 2093.
[5] Jeffrey and Vogel, *J.*, 1935, 21.

TABLE 2.

E.M.F. measurements.

Ni malonate

Experiment	1	2	3	4	5	6
10^3m_1	6·9953	8·8309	8·6658	9·3783	9·3888	7·3344
10^3m_2	7·0910	8·9586	8·9599	9·4576	12·279	10·138
10^3m_3	6·7447	8·9607	8·3882	10·1045	7·7463	9·0442

Expt.	$(E - E°)$	10^3I	10^4[H$^+$]	10^3[HMal$^-$]	10^5[Mal^{2-}]	10^3[MMal]	$10^{-4}K$
			At 0°				
1	0·29919	24·15	2·994	4·901	6·277	1·182	1·09
2	0·28985	31·54	3·465	6·020	7·120	1·571	1·09
3	0·29961	29·85	3·056	5·998	7·930	1·654	1·02
4	0·28623	35·23	3·666	6·359	7·320	1·660	1·04
5	0·32227	26·58	0·9893	5·749	22·80	3·086	0·98
6	0·31968	28·72	0·9554	4·023	16·86$_5$	2·925	0·99
						Mean	1·03 ± 0·04
			At 15°				
1	0·31503	24·21	3·088	4·953	6·193$_5$	1·161$_5$	1·11
2	0·30447	31·54	3·678	6·037	6·781	1·577	1·19
3	0·30904	29·87	3·220	6·026	7·620	1·552	1·09
4	0·30067	35·27	3·860	6·396	7·057	1·653	1·11
5	0·33876	26·55	1·046	5·756$_5$	21·75	3·096	1·06
6	0·33612	28·66	1·006	4·008	16·05	2·955	1·09
						Mean	1·11 ± 0·02
			At 25°				
1	0·32539	24·20	3·176	4·958	5·779	1·168	1·22
2	0·31444	31·53	3·790	6·042	6·325	1·584	1·32
3	0·31917	29·83	3·342	6·018	7·035	1·577	1·24
4	0·31052	35·28	3·975	6·419	6·606	1·641	1·21
5	0·34994	26·50	1·075	5·760	20·27	3·395	1·35
6	0·34714	28·62	1·037	4·007	14·91	2·978	1·21
						Mean	1·26 ± 0·04
			At 35°				
1	0·33604	24·16	3·220	4·945$_5$	5·306	1·180	1·37
2	0·32474	31·48	3·843	6·027	5·814	1·599$_5$	(1·48)
3	0·32960	29·78	3·392	6·003	6·459	1·584	1·38
4	0·32065	35·20	4·040	6·384	6·047	1·678$_5$	1·39
5	0·36137	26·41	1·093$_5$	5·753	18·61$_5$	3·128	1·31
6	0·35842	28·56	1·057	4·001	13·67	2·984	1·36
						Mean	1·36 ± 0·03
			At 45°				
1	0·34702	24·11	3·231	4·928	4·776	1·195	1·59
2	0·33533	31·42	3·861	6·002	5·230	1·619	(1·71)
3	0·34032	29·71	3·411	5·978	5·806	1·603	1·60
4	0·33112	35·13	4·055	6·357	5·443	1·698	1·60
5	0·37295	26·32	1·105	5·739	16·64	3·159	1·52
6	0·36982	28·48	1·072	3·990$_5$	12·18	3·005	1·57
						Mean	1·58 ± 0·02

Co malonate

Expt.	1	2	3	4	5	6	7
10^3m_1	7·4816	4·1495	6·9985	8·5901	13·088	8·7848	12·934
10^3m_2	13·055	7·3552	10·211	12·738	18·767	12·977	18·574
10^3m_3	5·8042	2·0758	5·8160	7·2657	9·7605	7·0612	9·2960

Expt.	8	9	10	11	12	13	14
10^3m_1	7·0661	16·427	6·7301	8·7975	8·0952	8·8666	13·016
10^3m_2	10·385	27·950	9·6357	11·997	9·7797	12·257	18·856
10^3m_3	5·5537	11·472	4·8647	6·8558	5·4218	7·0831	9·3630

Expt.	$(E - E°)$	10^3I	10^6[H$^+$]	10^3[HMal$^-$]	10^3[Mal^{2-}]	10^3[MMal]	$10^{-3}K$
			At 0°				
1	0·40023	19·69	4·640	1·893	1·491	4·092	4·68
2	0·44449	10·47	1·860	0·9397	1·628	1·581	4·43
3	0·36281	20·19	22·78	3·664	0·5914$_5$	2·694	4·31
5	0·34301	34·09	33·58	7·111	0·8856	4·959	4·45
7	0·34637	32·99	3·015	7·028	0·9666	4·822	4·19
8	0·36734	19·63	1·962	3·643	0·6785	2·702	4·07
						Mean	4·36 ± 0·15

TABLE 2. (*Continued.*)

Expt.	$(E - E^\circ)$	10^3I	$10^6[H^+]$	$10^3[HMal^-]$	$10^3[Mal^{2-}]$	$10^3[MMal]$	$10^{-3}K$
			At 15°				
1	0·42118	19·40	4·862	1·893	1·426	4·157	5·26
2	0·46867	10·40	1·883	0·9398	1·608	1·601	4·82
4	0·37518	24·48	25·46	4·300	0·6539	3·578	4·93
5	0·36025	33·87	36·07	7·110	0·8302	5·016	5·01
6	0·37773	24·28	2·362	4·456	0·7292	3·543	4·57
7	0·36404	32·75	3·236	7·027	0·9064	4·883	4·71
8	0·38599	19·47	2·097	3·642	0·6368	2·745	4·57
9	0·39489	38·70	7·744	4·860	2·742	8·807	5·10
						Mean	4·87 ± 0·20
			At 25°				
2	0·48566	10·24	1·836	9·400	1·572	1·636	5·50
4	0·38726	24·26	26·53	4·298	0·5996	3·634	5·63
5	0·37190	33·60	37·47	7·109	0·7648	5·083	5·69
9	0·40875	38·24	7·733	4·861	2·628	8·921	5·73
10	0·39819	17·35	24·88	3·702	0·5086$_5$	2·470	5·84
11	0·37511	24·25	45·10	5·306	0·4353	2·933	5·80
12	0·36553	21·12	81·06	5·833	0·2574	1·756	5·87
13	0·37609	24·75	42·13	5·208	0·4597	3·086	5·72
14	0·37584	32·18	33·31	6·913	0·8267	5·162	5·81
						Mean	5·73 ± 0·10
			At 35°				
1	0·45067$_5$	18·81	4·843	1·894	1·272	4·312	6·92
2	0·50330$_5$	10·09	1·747	0·9404	1·534	1·674	6·36
4	0·39868	23·95	28·23	4·290	0·5243	3·714	6·84
5	0·38268	33·20	39·83	7·092	0·6700	5·187	6·91
10	0·41105	17·16	25·42	3·699	0·4631	2·518	6·76
11	0·38720	24·08	46·14	5·301	0·3968	2·974	6·64
12	0·37728	21·00	83·33	5·822	0·2332	1·788	6·77
13	0·38861	24·62	42·46	5·208	0·4260	3·120	6·42
14	0·38799	31·90	34·18	6·909	0·7585	5·232	6·77
						Mean	6·71 ± 0·16
			At 45°				
1	0·46590	18·39	4·750	1·894	1·167	4·416	8·37
2	0·52145	9·84	1·638	0·9404	1·472	1·737	8·20
4	0·41052	23·65	29·51	4·282	0·4522	3·791	8·40
5	0·39435	32·82	41·42	7·077	0·5818	5·284	8·44
9	0·43752	36·97	7·422	4·863	2·234	9·238	7·98
10	0·42410	16·95	25·79	3·696	0·4117$_5$	2·571	8·06
11	0·39919	23·88	47·34	5·291	0·3492$_5$	3·028	7·93
12	0·38908	20·86	85·09	5·805	0·2060	1·788	7·81
14	0·40034	31·55	34·51	6·903	0·6735	5·321	7·94
						Mean	8·12 ± 0·20

Mn malonate

Expt.	1	2	3	4	5	6
10^3m_1	9·7405	4·9059	13·203	17·155	5·4812	12·251
10^3m_2	14·747	9·1704	21·641	32·661	8·3848	17·950
10^3m_3	8·0559	6·0045	10·124	13·708	5·0717	8·4660

Expt.	7	8	9	10	11
10^3m_1	8·8670	16·797$_5$	7·7085	8·0905	13·903
10^3m_2	13·092$_5$	28·171	9·4930	10·452	14·701
10^3m_3	7·1210	11·220	9·1815	10·215	14·018$_5$

Expt.	$(E - E^\circ)$	10^3I	$10^5[H^+]$	$10^3[HMal^-]$	$10^4[Mal^{2-}]$	$10^3[MMal]$	$10^{-3}K$
			At 0°				
1	0·37534	31·30	1·019	4·671	1·876	3·167	1·26
2	0·42751	21·06	0·1419	0·6375	1·668	2·600	1·38
3	0·38229	39·90	0·6233	4·733	3·313	5·144	1·30
4	0·41632	55·03	0·1135	1·647	6·943	8·565	1·20
9	0·33713	33·20	4·567	5·594	0·5088	1·464	1·40
						Mean	1·31 ± 0·06
			At 15°				
1	0·39353	30·57	1·128	4·668	1·695	3·350	1·56
2	0·45045	20·92	0·1459	0·6388	1·633	2·634	1·47
3	0·40114	38·77	0·6825	4·731	3·030	5·428	1·62
4	0·43783	53·51	0·1206	1·647	6·562	8·945	1·46

TABLE 2. (*Continued.*)

Expt.	$(E - E°)$	$10^3 I$	$10^5[H^+]$	$10^3[HMal^-]$	$10^4[Mal^{2-}]$	$10^3[MMal]$	$10^{-3}K$
				At 15°			
5	0·41062	19·21	0·8506	2·545	1·094	$1·830_5$	1·53
6	0·38794	34·07	1·365	6·449	1·994	3·763	1·58
7	0·39373	27·50	1·248	4·569	1·459	2·809	1·57
8	0·40447	45·58	0·5509	$5·389_5$	4·480	6·913	1·66
						Mean	1·56 ± 0·05
				At 25°			
5	0·42385	18·83	0·8872	2·545	0·9987	1·926	1·83
6	0·40051	33·41	1·417	6·448	1·831	3·927	1·89
7	0·40643	27·01	1·299	4·568	1·337	2·931	1·87
8	0·41841	44·64	0·5551	5·390	4·247	$7·146_5$	1·95
9	0·36378	32·76	5·444	5·569	$4·095_5$	1·580	2·01
10	0·36661	35·58	$4·433_5$	5·448	5·033	2·021	2·03
						Mean	1·93 ± 0·07
				At 35°			
5	0·43672	18·35	0·9347	2·543	0·8795	2·046	2·32
6	0·41321	36·70	1·461	6·445	1·653	4·107	2·31
7	0·41871	26·37	1·370	4·564	1·178	3·093	2·35
8	0·43236	43·36	0·5581	5·390	3·926	7·467	2·41
9	0·37491	32·56	5·697	5·555	3·650	1·632	2·39
10	0·37779	35·34	4·646	5·437	4·480	2·083	2·41
						Mean	2·37 ± 0·04
				At 45°			
5	0·45009	17·90	0·9647	$2·541_5$	0·7666	2·160	2·94
6	0·42573	31·82	1·514	6·440	1·437	4·326	2·97
7	0·43140	25·75	1·420	4·561	1·024	3·249	2·98
9	0·38634	32·36	5·886	$5·540_5$	3·194	1·686	2·91
10	0·38922	35·09	4·816	5·424	3·906	2·148	2·94
11	0·34622	52·21	17·90	11·09	2·426	1·653	3·03
						Mean	2·96 ± 0·03

Concentrations were chosen so as to exclude complex species of the type $MHMal^+$ which have very much smaller association constants.[6] The results are given in Table 2 which shows the good constancy of K. At 25°, the values are in excellent agreement with K(NiMal) = $1·3 \times 10^4$, K(CoMal) = $5·3 \times 10^3$, and K(MnMal) = $1·95 \times 10^3$ obtained from colorimetric pH measurements.[7] Plots of log K against T^{-1} in Fig. 1 show marked curvatures and, as was found with the oxalates, ΔC_p values are considerable. The equation $\log K = a + bT + cT^2$ fits the results with a maximum difference between calculated and experimental K values of 3%. The values of the parameters calculated from results at 0°, 15°, and 45° are:

	a	$-10^2 b$	$10^5 c$
NiMal	8·821	3·549	6·548
CoMal	10·117	4·923	9·341
MnMal	9·119	4·759	9·378

The thermodynamic properties, ΔG ($= -\boldsymbol{R}T \ln K$), ΔH ($=2·303\boldsymbol{R}T^2[b + 2cT]$), ΔC_p ($=4·606\boldsymbol{R}T[b + 3CT]$), and ΔS ($=[\Delta H - \Delta G]/T$) are given in Table 3. Uncertainties were estimated by using different combinations of experimental results at three temperatures for the calculation of a, b, and c. $-\Delta G$ is consistently lower than the corresponding oxalate values and reflects the lower stability of the six-membered ring. A larger ΔH for the malonates, however, makes ΔS almost the same as that for the oxalates.

TABLE 3.
Thermodynamic properties.

Reaction	ΔH (kcal. mole^{-1})	ΔG_{298} (kcal. mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	ΔC_p (cal. deg.$^{-1}$)
$Ni^{2+} + Mal^{2-}$	1·77 ± 0·1	−5·60 ± 0·02	24·8 ± 0·3	46 ± 20
$Co^{2+} + Mal^{2-}$	2·57 ± 0·1	−5·13 ± 0·02	25·8 ± 0·3	68 ± 25
$Mn^{2+} + Mal^{2-}$	3·53 ± 0·2	−4·48 ± 0·02	26·8 ± 0·7	92 ± 30

[6] Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314.
[7] Stock and Davies, *J.*, 1949, 1371.

The calculation of the entropy of hydration of the complexes from

$$\Delta S_{hyd}(MMal) = \Delta S - \Delta S_g + \Delta S_{hyd}(M^{2+}) + \Delta S_{hyd}(Mal^{2-}),$$

where ΔS_g and ΔS_{hyd} are gaseous and hydration entropies, respectively, was made as described in Part VII; the values are given in Table 4. $\Delta S_{hyd}(MMal)$ is lower than the

TABLE 4.

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

Ion pair	S_g (MMal)	ΔS	$S°$ (MMal)	$-\Delta S_{hyd}$ (MMal)	r_+^{-1} (Å^{-1})
NiMal	70·3	24·8	7·3	63·0	1·37
CoMal	70·3	25·8	9·3	61·0	1·35
MnMal	70·2	26·8	12·3	57·9	1·28

corresponding oxalate values (—54·8 to —56·1 cal. deg.$^{-1}$ mole^{-1}) and this may be due to a greater neutralisation of charge accompanying the formation of the oxalate complexes. Frequently association entropies are correlated with properties of the ions taking part in the reactions, no corrections being made for the different translation and rotational entropy contributions. The importance of using only the hydration entropies of the ion-pairs in such comparisons [8] is seen in Table 4. The small changes in $\Delta S_{hyd}(MMal)$ are in the expected direction with r_+^{-1} even though ΔS varies in the opposite sense.

Changes in ΔH account for the differences of stability over the series of cations and, as with the oxalates, there is a regular change in ΔH in reverse order to changes in ionisation potential I_{02}, r_+^{-1}, and $-\Delta H_{hyd}(M^{2+})$.

We thank Wilmot Breedon for the award of a fellowship to V. S. K. N., and Mr. I. R. Desai for assistance with some of the experimental work.

COLLEGE OF ADVANCED TECHNOLOGY, GOSTA GREEN, BIRMINGHAM, 4.
CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW, W.2. [*Received, April* 13*th*, 1961.]

[8] Nancollas, *Quart. Rev.*, 1960, **14**, 402.