455. Studies on Metal Complexes in Solution. Part I. Phthalates of Some Transition Metals.

By I. R. DESAI and V. S. K. NAIR.

Thermodynamic stability constants of the 1:1 complexes of manganese, cobalt, and nickel ions with the phthalate ion have been determined by a precise potentiometric method employing a Harned-type cell, at temperatures in the range $0-45^{\circ}$. The thermodynamic quantities, ΔG , ΔH , and ΔS for the reaction $M^{2+} + o-C_6H_4(CO_2)_2^{2-} \iff o-C_6H_4(CO_2)_2M$, have been derived. Also from the variation of ΔH with temperature, ΔC_p for the reaction has been estimated.

IN other studies on the thermodynamics of ion association,¹ ion pairs of relatively low stability have been investigated. We have extended the studies to more stable complexes of chelate type and followed the effects of substitution and configurational factors on the thermodynamic properties of the complexes. Of the aromatic bivalent anions, phthalate was chosen because it is available in a pure form and because of the fairly high solubility of its complexes with bivalent metals. By taking a higher proportion of M^{2+} to phthalate, species such as $M[C_6H_4(CO_2)_2]_2^{2-}$ can be avoided, and the study limited to the 1 : 1 species. The Harned-type cell

H₂,Pt|KHphthalate,MCl₂|AgCl|Ag

has been used for studying manganese, cobalt, and nickel phthalates.

¹ Nancollas, J., 1955, 1458.

EXPERIMENTAL

Stock solutions prepared from "AnalaR" metal chlorides were standardised by gravimetric analysis as silver chloride; agreement between duplicate estimations was better than $\pm 0.02\%$. Stock solutions of "AnalaR" potassium hydrogen phthalate were prepared by weight. Exactly 0.01m-hydrochloric acid, prepared from constant-boiling acid, was used in the standardisation of the silver-silver chloride electrodes prepared as described before.² The apparatus and procedure were similar to those described previously.² Equilibrium was attained only very slowly at the start of each run, so the cells were left overnight at 0° to come to equilibrium and the experiments completed for other temperatures the following day. Once equilibrium had been obtained at one temperature 1.5 hours were required for a constant e.m.f. to be reached at another temperature. E.m.f. readings remained constant within 30 µv for more than 0.5 hr. Since there was no drift in the e.m.f. the chance of interaction between the phthalate and the hydrogen was discounted.

RESULTS AND DISCUSSION

Accurate values for the dissociation of phthalic acid over the range 0-60° are available from the work of Hamer et al.3 who used the cell *

H₂,Pd|H₂Ph, KHPh (or KHPh, K₂Ph),KCl|AgCl(s)|Ag(s)

The values of the thermodynamic dissociation constants of phthalic acid obtained by them and used in this work are given in Table 1. In the cell

 $H_2,Pt|KHPh(m_1),MCl_2(m_2)|AgCl|Ag$

the concentration of hydrogen ions is given by

$$-\log \left[\mathrm{H}^{+}\right] = (E - E^{0})/k + \log_{10} 2m_{2} + \log_{10} \gamma_{\mathrm{H}} + \gamma_{\mathrm{Cl}} -$$

where E is the corrected e.m.f., m represents molality, k = 2.3026 RT/F, and γ is activity coefficient. For the concentrations of various ionic species one can write

$$m_1 = [H_2Ph] + [HPh^-] + [Ph^{2-}] + [MPh],$$

and $m_2 = [M^{2+}] + [MPh].$

TABLE 1.

Thermodynamic dissociation constant of phthalic acid.

	-					
	Temp.	0°	15°	25°	3 5°	45°
$10^{3}K_{1}$		1.190	1.157	1.123	1.078	1.027
$10^6 K_2^{-1}$		3 ∙696	3.934	3.906	3 ·740	3.454

For electroneutrality,

 $[H^+] + 2[M^{2+}] + m_1 = 2m_2 + [HPh^-] + 2[Ph^{2-}] + [OH^-],$

in which [OH⁻] is negligible at the pH's obtained.

 K_1 and K_2 are the thermodynamic first and second dissociation constants of phthalic acid. Brannan and Nancollas⁴ have shown that for ion association between nickel and substituted malonate ions the Davies equation ⁵

$$-\log \gamma_z = A z^2 [I^{\frac{1}{2}}/(1+I^{\frac{1}{2}}) - 0.2I]$$

can be used for computing activity coefficients up to an ionic strength of 0.2m. In the present work, therefore, I being always less than 0.1m, the Davies equation has been used. Ionic strength,

$$I = \frac{1}{2} \{ [\mathrm{H}^+] + 6m_2 - 3m_1 + [\mathrm{HPh}^-](5 + 8K_2/[\mathrm{H}^+]\gamma_2 + 4[\mathrm{H}^+]\gamma_1^2/K_1) \}$$

* Throughout this paper, Ph denotes phthalate.

- ² Nair and Nancollas, J., 1958, 4144. ³ Hamer, Pinching, and Acree, J. Res. Nat. Bur. Stand., 1945, 35, 539; Hamer and Acree, *ibid.*, p. 381.
 - ⁴ Brannan and Nancollas, Trans. Faraday Soc., 1962, 58, 354.

⁵ Davies, J., 1938, 2093.

Successive approximations of the above equations to constant ionic strength enabled the various ionic concentrations to be evaluated; the stability constant of MPh was calculated from the relation

$$K = [MPh]/[M^{2+}][Ph^{2-}]\gamma_2^2.$$

Table 2 gives the results for manganese, cobalt, and nickel phthalates for all temperatures; the last column shows the constancy of the K values. At any one temperature the deviation among the K values is always less than 1%. There are only very scanty recorded data on stability constants of bivalent metal phthalates; * as would be expected the $\log_{10} K$ values of all these three transition-metal ions are higher than the corresponding values for barium (2.33) and calcium ⁷ (2.43) at 25°. The K values increase in the order Mn < Co < Ni, as observed by Irving and Williams ⁸ for a large number of ligands.

			•	Fable 2 .			
			Mang	anese phthalate			
		1	2	3	4	5	6
	$10^{3}m_{1}$	8.9623	12.942	16·490	9.9301	13.784	17.939
	$10^3 m_2$	8.8445	9.4789	11.425	8.9468	10.598	$12 \cdot 487$
	$(E - E_0)$	10³I	$10^{4}[H^{+}]$	10 ³ [HPh-]	10^{4} [Ph ²⁻]	10^{4} [MPh]	K
				At 0°			
1.	0.31163	34.85	1.410	7.545	3.882	3.909	(461)
2.	0.30947	40·49	1.472	10.908	5.602	5.306	`444 ´
3.	0.30417	49.53	1.573	$13 \cdot 845$	7.041	6.971	434
4.	0.31163	36.14	1.401	8·387 ₅	4.387	4.026	423
5.	0.30637	44.57	1.522	11.587	5.910	5.8385	437
6.	0.30170	54.00	1.620	15.031	7.617	7.734	429
			·				$433 \cdot 4 \pm 3$
				At 15°			
1.	0.32802	34.81	1.463	7.479	4.030	4 ·116	483
2.	0.32538	40.35	1.550	10.787	5.718	5.834	497
3.	0.31983	49.36	1.656	13.689	7.201	7.629_{5}	484
4.	0.32761	36·03	1.477	8·293	4.467	4.457	477
5.	0.32209	44·41	1.604	11.454	6.028	6.423	490
6.	0.31715	53.79	1.709	14.855	7.767	8.509	483
							485.7 ± 2.6
				At 25°			
1.	0.33920	34.72	1.484	$7 \cdot 432$	3 ⋅958	4·436	544
2.	0.33646	40.21	1.571	10.718	5.622	6.283	560
3.	0.33076	49.19	1.677	13.604	7.093	8.173	542
4.	0.33869	35.90	1.503	8.236	4.371	4.851	545
5.	0.33281	44.20	1.643	11.360	5.854	7.089	574
6.	0.32798	5 3 ·60	1.733	14.758	7.644	9.128	543
							$551 \cdot 3 + 5 \cdot 2$
				At 3 5°			
1.	0.35076	34.59	1.481	7.393	3.810	4.776	626
2.	0.34822	40 ·10	1.553	10.679	5.476	6.615_{5}	623
3.	0.34200	48 ·96	1.678	13.524	6.814	8·854 [°]	631
4.	0.35039	35.80	$1 \cdot 492$	$8 \cdot 201$	4.237	5.156	614
5.	0.34468	44·13	1.610	11.337	5.769	7.273	614
6.	0.33934	$53 \cdot 41$	1.720_{5}	14.692	7.418	9.678	612
			v				620.0 ± 3.3
				At 45°			
1.	0.36287	34 ·48	1.451	7.368	3·618 ₅	5.080	720
2.	0.36007	39.89	1.532	10.628	5.160	7.176	739
3.	0.35360	48 .69	1.659	$13 \cdot 451$	6·409	9.613	754
4.	0.36222	35.63	1.476	8.158	3.977	5.622	735
5.	0.35633	43.90	1.593	11.275	5.417	7.926	736
6.	0.35078	53·09	1·706 [°]	14.602	6.956	10.568	738
							737.0 ± 3.3

* For nickel a value of 2.14 for $\log_{10} K$ at I = 0.1M has been reported ⁶ (which corresponds to the value for $\log_{10} K$ of 3.02) at 25° from a pH-titration method.

⁶ Yasuda, Suzuki, and Yamasaki, J. Phys. Chem., 1956, 60, 1649.

⁷ Topp and Davies, J., 1940, 87.
⁸ Irving and Williams, J., 1953, 3192.

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$\begin{array}{c c c c c c c c c c c c c c c c c c c $				TABLE 2	. (Contini	ied).			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				Cob	alt phthalate				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1	2	3	4	5	6	7	8
	${10^3m_1 \over 10^3m_2}$	$\dots 6.9630 \\ \dots 5.3403$	8·7632 7·0530	$12.675 \\ 9.1875$	$16.202 \\ 11.236$	$7 \cdot 4545 \\ 5 \cdot 8412$	9·7523 8·9269	14·563 10·940	$17.104 \\ 12.051$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$(E - E_0)$	10³ <i>I</i>	$10^{4}[H^{+}]$	10 ³ [HPh-]	10^4 [Ph ⁴	²⁻] 10 ⁴ [M	[Ph]	K
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					At 0°				
2. 0'31085 29'30 1384 1'310 3'033 3'330 300 300 3. 0'3085 39'30 21 564 10.566 5'033 6'376 (596) 4. 0'30303 48'32 1673 13'453 6'3854 8'194 571 5. 0'32271 24'02 1'275 6'316 3'2874 4'040 (540) 6. 0'30957 45'83 1.667 12'071 5'666 7'223 (596) 8. 0'3014 51'48 1'706 14'184 6'729 8'223 538 4'927 581 7. 0'30367 45'83 1.667 12'071 5'666 7'223 (596) ± 357 1. 0'3375 22'51 1'305 5'847 3'157 3'077 618 2. 0'33038 29'17 1'447 7'297 3'791 4'2614 616 3. 0'3375 29'17 1'467 7'297 3'791 4'2614 616 5. 0'32375 32'45' 1'570 8'464 4'040 5'779 623 7. 0'31945 45'72 1'736 11'951 3'115 3'286 6'84 (690) 6. 0'3237 3'51 1'570 8'464 4'040 5'779 6'22 7. 0'31945 45'72 1'736 11'951 3'115 3'286 6'84 6'20 7. 0'31945 45'72 1'736 11'951 3'115 3'286 6'84 6'20 7. 0'31945 45'72 1'736 11'951 3'115 3'286 6'84 6'20 7. 0'33081 3'8'65 1'6'29 10'419 5'223 6'737 6'22 7. 0'31945 45'72 1'736 11'951 3'115 3'286 6'84 6'70 4t 25° 7. 0'31945 45'72 1'736 11'951 3'115 3'286 6'84 6'70 4t 35° 7. 0'33062 45'62 1'742 11'892 5'836 5'79 3'099 3'608 7'74 4. 0'32984 4'7.99 1'761 13'238 6'255 9'173 6'70 5. 0'35107 24'38 1'350 6'177 3'315 3'155 6'690 5'597 6'93 7. 0'33062 45'62 1'742 11'892 5'836 '8'87 6'79 7. 0'33062 45'62 1'742 11'892 5'836 '8'87 6'79 7. 0'33062 45'62 1'742 11'892 5'836 '8'87 6'79 7. 0'33062 45'62 1'76'2 10'366 5'037 7'232 7'6'5 4. 0'34121 4'7'80 1'752 13'171 6'312 9'716 7'57 5. 0'36307 2'2'39 1'345 6'187 3'193 3'815 7'55 6. 0'34871 3'530 1'590 7'956 3'841 5'534 7'53 7. 0'34205 45'47 1'730 11'836 5'659 1'6'31 9'716 7'57 5. 0'3604 3'8'52 1'597 10'317 4'755 7'834 8'95 1. 0'3764 5'2'19 1'319 5'741 2'753 4'015 (995) 7. 0'33064 3'8'52 1'597 10'317 4'755 7'834 8'95 10'377 10'664 4'681 7'834 8'95 10'378 1'2'2'1 1'319 5'741 2'753 1'0'16'8 8'901 1'1'4'4'77 7'68 8. 0'35057 7'0'72 1'758 5'953 2'856 3'737 (7'18) 7. 0'3153 2'562 1'703 11'780 5'345 9'111' 11'849 1'3'265 10'377 10'664 4'681 7'897 7'67 1'40 1'757 5'75 4'40 9'858 7'757 1'75 1'10'16'14'19' 10'124'19' 19'255 10'376 1'2'2'2'1'452	1.	0.32519	22.58	1.243	5.908	3.093	2.80	02 557	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2. 3	0.31085	29.25	1.384	7.376	3.093	3.93	30 202 76 (506)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4 .	0.30303	48·26	1.673	13.453	6.385	8.19	34 571	
	5.	0.32271	24.52	1.275	6.316	3.287	3 ∙04	40 (540)	
7. 0.30357 45.83 1.667 12.071 5.666 7.625 (595) 8. 0.30114 51.48 1.706 14.184 6.729 5.723 555 566.4 \pm 3.8 At 15° 1. 0.34199 22.51 1.305 5.847 3.157 3.077 618 2. 0.3332 29.17 1.447 7.297 3.791 4.261 ₄ 616 3. 0.32478 38.92 1.630 10.462 5.220 6.664 636 4. 0.3180 48.12 1.748 13.12 6.583 8.740 615 5. 0.33938 24.45 1.339 6.250 3.357 3.334 (599) 6. 0.32597 3.551 1.579 8.046 4.040 5.279 628 7. 0.31945 45.72 1.736 11.951 5.862 ₈ 8.067 632 7. 0.31945 45.72 1.736 11.951 5.862 ₈ 8.067 632 7. 0.31945 45.72 1.736 11.951 5.862 ₅ 9.173 670 6. 0.35217 3.551 1.629 10.419 5.229, 6.881 670 4. 0.32984 47.99 1.761 13.238 5.225 9.173 670 6. 0.33714 35.41 1.597 7.943 5.255 9.173 670 6. 0.33714 35.41 1.597 7.943 5.583 8.857 679 7. 0.33062 45.62 1.742 11.892 5.836 8.827 7. 0.33062 45.62 1.742 11.892 5.836 8.837 679 7. 0.33062 45.62 1.742 11.892 5.836 8.8387 679 7. 0.33062 45.62 1.730 1.732 13.171 6.312 9.716 757 7. 0.34005 45.71 1.462 10.366 5.037 7.323 765 7. 0.34005 45.71 1.452 10.376 6.3841_8 5.963 774 2. 0.36566 28.97 1.467 7.219 3.602 4.847_8 776 7. 0.34205 45.47 1.730 11.836 5.656 8.842 761 7. 0.34205 45.47 1.730 11.836 5.963 744 7. 0.34205 45.47 1.730 11.836 5.963 744 7. 0.34205 45.47 1.730 11.836 5.963 8.841_8 5.963 7. 0.34205 45.75 1.725 13.171 6.312 9.716 755 7. 0.34205 45.74 1.730 11.836 5.963 7.918 8.916 7. 0.35376 4.526 1.703 11.780 5.345 9.418 8.86 8. 0.35064 38.52 1.507 10.317 4.755 7.834 895 7. 0.34205 45.75 1.725 13.108 5.963 9.418 8.86 8. 0.35064 38.52 1.507 10.317 4.755 7.834 895 7. 0.34205 45.75 1.725 13.108 5.943 9.418 8.86 8. 0.35064 38.52 1.507 10.317 4.755 7.834 895 7. 0.35376 4.526 1.703 11.780 5.345 9.418 8.86 8. 0.35065 35.15 1.566 7.916 8.911 11.848 186 7. 0.35376 4.526 1.703 11.780 5.345 9.418 8.86 8. 0.35065 35.15 1.568 7.916 8.911 11.1848 18.86 8. 0.35064 38.52 1.507 10.317 4.755 7.784 1. 0.31853 2.562 1.438 6.593 2.8	6.	0.30987	35.60	1.510	8.132	3.928	4.92	27 581	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	7. e	0.30357	45.83	1.667	12.071	5.666	7.62	25 (595)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.	0.20114	51.40	1.100	14.104	0.125	0.12	566.4	4 ± 3·8
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					At 15°				_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.	0.34199	22.51	1.305	5.847	3.157	3.07	618	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.	0.33332	29.17	1.447	7.297	3.791	4.26	$51_5 616$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	а. 4.	0.31880	30.92 48.12	1.030	10.402	5·220 6·583	8.74	04 030 LO 615	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5.	0.33938	24.45	1.339	6.250	3.357	3.33	34 (599)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6.	0.32597	35.51	1.579	8.046	4 ·040	5.27	79 `628´	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	7.	0.31945	45.72	1.736	11.951	5.862_{s}	s 8∙06	632 632	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					At 25°			024.2	2 ± 3.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.	0.35375	22.44	1.317	5.815	3.115	3.28	86 684	
3. 0.33621 38.85 1.629 10.419 5.229, 6.881 670 4. 0.32984 47.99 1.761 13.238 6.525 9.173 670 5. 0.35107 24.38 1.350 6.217 3.315 3.545 660 6. 0.33714 35.41 1.597 7.997 3.980 5.597 693 7. 0.33062 45.62 1.742 11.892 5.836 8.837 679 677.0 \pm 4.4 1. 0.36591 22.36 1.308 5.790 3.009 3.508 774 2. 0.36656 28.97 1.457 7.219 3.602 4.847 ₈ 776 3. 0.34776 38.71 1.622 10.366 5.037 7.323 765 4. 0.34121 47.80 1.752 13.171 6.312 9.716 757 5. 0.36307 24.29 1.345 6.187 3.193 3.815 755 6. 0.34871 35.30 1.590 7.956 3.841 ₈ 5.934 783 7. 0.34205 45.47 1.730 11.836 5.656 8.842 761 767.3 \pm 4.57 1. 0.37768 22.19 1.319 5.741 2.753 ₈ 4.015 (995) 2. 0.36877 28.85 1.431 7.190 3.406 5.178 900 3. 0.35964 38.62 1.597 10.317 4.755 7.834 895 4. 0.35289 47.57 1.725 13.108 5.963 10.368, 884 5. 0.37546 24.18 1.322 6.163 3.9016 4.105 883 6. 0.36056 35.15 1.569 7.916 3.6017 6.348 916 7. 0.33376 42.418 1.322 6.163 3.9016 4.105 883 6. 0.36056 35.15 1.569 7.916 3.6017 6.348 916 7. 0.33376 45.26 1.703 11.780 5.345 9.418 886 7. 0.36056 35.15 1.569 7.916 3.617 6.348 916 7. 0.36375 45.22 1.90 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₁ 7.1319 ₅ 7.8720 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₁ 7.1319 ₅ 7.8720 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₁ 7.1319 ₅ 7.8720 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₁ 7.1319 ₅ 7.8720 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₁ 7.1319 ₅ 7.8720 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₂ 6.3958 7.2020 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₂ 6.3958 7.2020 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₂ 6.3958 7.2020 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₂ 6.3958 7.2020 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₂ 6.3958 7.2020 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₂ 6.3958 7.2020 13.006 15.599 7.6567 9.1425 14.077 16.153 10 ³ m ₂ 6.3958 7.2020 13.006 15.599 7.6567 9.1425 14.077 16.153 1.03088 41.83 1.737 10.664 4.681 7.897 787	2.	0.34474	$\bar{29} \cdot \bar{08}$	1.463	7.255	3.736	4.53	88 682	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.	0.33621	38.85	1.629	10.419	$5 \cdot 229_{s}$	6.88	81 670	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 .	0.32984	47.99	1.761	13.238	6.525	9.17	73 670	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5. 6.	0.33714	24·38 35·41	1.350	0·217 7·997	3.315	3·04 5•50	ED 000 17 693	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	7.	0.33062	45.62	1.742	11.892	5.836	8.38	679	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $								677.0	0 ± 4.4
1. 0.36591 22.36 1308 5.790 3.009 3.508 774 2. 0.36565 28.97 1.457 7.219 3.602 4.8475 776 3. 0.34776 38.71 1.622 10.366 5.037 7.323 765 4. 0.34121 47.80 1.752 13.171 6.312 9.716 757 5. 0.36307 24.29 1.345 6.187 3.193 3.815 755 6. 0.34871 35.30 1.590 7.956 3.8415 5.934 783 7. 0.34205 45.47 1.730 11.836 5.656 8.842 761 767.3 ± 4.5 767.3 ± 4.5 1. 0.37768 22.19 1.319 5.741 2.7535 4.015 (995) 2. 0.36877 28.85 1.431 7.190 3.406 5.178 900 3. 0.35964 38.52 1.597 10.317 4.755 7.834 895 4. 0.35289 47.57 1.725 13.108 5.963 10.3688 884 5. 0.37546 24.18 1.322 6.163 3.016 4.105 883 6. 0.36056 35.15 1.569 7.916 3.617 6.348 916 7. 0.35376 45.26 1.703 11.780 5.345 9.418 886 8. 0.35057 50.72 1.768 13.806 6.253 11.123 878 8. 0.35057 50.72 1.768 13.266 7 8.111 11.849 13.265 ($E - E_{0}$) $10^{3}I$ $10^{4}[H^+]$ $10^{8}[HPh^-]$ $10^{4}[Ph^{2-]}$ $10^{4}[MPh]$ K At 0° 1. 0.31853 25.62 1.398 5.953 2.856 3.737 (718) 2. 0.31451 28.59 1.493 6.524 3.011 4.477 768 3. 0.30398 41.83 1.737 10.664 4.681 7.897 767 4. 0.29863 50.16 1.859 12.717 5.494 9.845 753 5. 0.31640 27.22 1.452 6.366 2.984 4.194 751 6. 0.30816 34.70 1.621 7.518 3.3615 5.573 766 7. 0.29948 47.59 1.841 11.467 4.926 9.047 771 8. 0.29048 53.57 1.909 13.131 5.632 10.432 746 760 ± 4.4	,	0.00501	22.84	1.000	At 35°	• • • • •			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1. 2	0.35656	22·36 28·07	1.308	5·790 7.910	3.609	3.50)8 774 17 776	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2. 3.	0.34776	38.71	1.622	10.366	5.037	7.32	23 765	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4.	0.34121	47.80	1.752	13.171	6.312	9.7	16 757	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5.	0.36307	24·29	1.345	6.187	3.193	3.81	5 755	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	6. 7	0.34871	35.30	1.590	7.956	3.841	5.93	84 783	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1.	0.94200	40.47	1.730	11.990	9.090	0.94	101 767.	3 + 4.5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					At 45°				·
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.	0.37768	22.19	1.319	5.741	2.753	<u>4</u> ∙01	l5 (995)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.	0.36877	28.85	1.431	7.190	3.406	5.17	78 900	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	J. 4.	0.35289	47.57	1.597	13.108	4.755	7.83 10.36	14 890 18 884	
	5.	0.37546	24.18	1.322	6.163	3.016	4.10	5 883	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6.	0.36056	35.15	1.569	7.916	3.617	6·34	8 916	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	7.	0.35376	45·26	1.768	11.780	5.345	9.41	.8 886	
$Nickel \ phthalate$ $\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.	0.20001	30.72	1.108	13.800	0.293	11.12	/3 878 891√2	7 ± 5.1
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				Nicl	kel phthalate				. <u>т</u> от
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		1	2	3	4	5	6	7	8
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$10^{3}m_{1}$	7.1319 ₅	7.8720	13.006	15.599	7.6567	9.1425	14·077	16.153
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$10^{3}m_{2}$	6.3958	7.2026	10.185	12.261	6.7915	8.9111	11.849	13.265
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	($(E - E_0)$	10³I	10 ⁴ [H+]	10 ³ [HPh-]	10^{4} [Ph ²	-] 104[M	Ph]	K
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.01070			At 0°				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.	U-31853	25.62	1.398	5.953	2.856	3.73	87 (718)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3 .	0.30398	20-09 41·83	1.493	0°024 10•664	3.011 4.681	4.47	7 767	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4 .	0.29863	50.16	1.859	12.717	5.494	9.84	5 753	
	5.	0.31640	27.22	1.452	6.366	2.984	4.19	4 751	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	б. 7	0.30816	34·70	1.621	7.518	3·3615	5.57	3 766	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8.	0.29948	47.09 53.57	1·841 1.900	11·467 13.191	4·926 5.629	9·04 10.49	771 9 776	
					10 101	5 002	10 40	760 -	± 4·4

			TABLE	2. (Continue	d).		
				At 15°			
1.	0.33488	25.53	1.474	5.882	2.902	4.086	798
2.	0.33088	28.51	1.559	6.454	3 ⋅095	4.776	824
3.	0.31979	41.71	1.815	10.545	4.818	8·394	823
4.	0.31416	50.01	1.942	12.573	5.660	10.444	808
5.	0.33279	27.13	1.521	6.295	3.055	4.512	815
6.	0.32415	34.60	1.596	$7 \cdot 432$	$3 \cdot 450$	5.949	825
7.	0.31504	47.44	1.925	11.334	5.069	9.608	828
8.	0.31180	53.41	1.994	12.981	5.807	11.050	799
							815 ± 5.0
				At 25°			
1.	0.34637	25.46	1.489	5.846	2.858	4.314	876
2.	0.34222	$28 \cdot 43$	1.576	6.413	3.047	5.035	903
3.	0.33075	41.57	1.835	10.475	4.749_{5}	8.824	903
4.	0.32509	49.89	1.953	12.501	5.621	10.846	870
5.	0.34422	27.06	1.537	6.257	3.009	4.758	894
6.	0.33523	34.50	1.717	7.381	3·391₅	6.273	908
7.	0.32581	47.29	1.949	11.253	4·990	10.104	911
8.	0.32262	53.28	2.007	12.904	5.761	11.488	(863)
							895 ± 6.4
				At 35°			
1.	0.35821	25.37	1.483	5.816	2.752	4.570	987
2.	0.35392	28.33	1.563	6.379	2.919	5.327_{5}	1002
3.	0.34235	41.47	1.812	10.434	4.631_{5}	9·133 [™]	986
4.	0.33623	49.69	1.948	$12 \cdot 426$	5.419°	11.419	980
5.	0.35606	26.97	1.527	6.227	2.908	5.002	996
6.	0.34670	34.39	1.711	7.340	3.268	6.601_{5}	(1019)
7.	0.33723	47.17	1.926	11.208	4.865	10.444	995
8.	0.33363	53.07	2.006	12.820	5.540	12.126	981
							990 ± 3.5
				At 45°			
1.	0.37038	25.27	1.462	5.788	2.591	4.859	1144
2.	0 ·366 00	28.22	1.546	6.349	2.768	5.620	1169
3.	0.35400	41.27	1.788	10.377	4.360_{5}	9.679	1145
4.	0.34767	49.46	1.924	12.354	5.101	12.086	1139
5.	0.36817	26.86	1.505	6.197	2.739	5.309	1153
6.	0.35850	34.26	1.688	7·301 ₅	3.078	6.971	1175
7.	0.34870	46 ·96	1.902	11.143	4.579	11.043	1155
8.	0.34496	$52 \cdot 82$	1.984	12.742	5.210	12.835	1139
							1152.4 ± 5.3

The $\log_{10} K$ values of the oxalates,⁹ malonates,¹⁰ and succinates ¹¹ of manganese, cobalt, and nickel at 25°, along with those for the phthalates, are given in Table 3. The stabilities decrease along the series oxalate, malonate, and succinate, and the ring size increases from 5-membered to 7-membered. However, in the case of phthalate, steric effects favour the orientation of the two carboxyl groups nearer to each other in a planar structure, and the stability of the phthalate of each metal is greater than that of the corresponding succinate. Also, the increase in stability found for the oxalates and the

TABLE 3.

Stabilities of transition-metal dicarboxylates at 25°.

$\operatorname{Log_{10}} K$	Oxalate	Malonate	Succinate	Phthalate
Mn ²⁺	3.967	3.193	$2 \cdot 265$	2.741
Co ²⁺	4.791	3.758	2.217	$2 \cdot 831$
Ni ²⁺	5.158	4 ·100	2.344	2.952

malonates in the series Mn, Co, and Ni is observed for the phthalates but not for the succinates.

Plots of $\log_{10} K$ against T^{-1} shown in the Figure are not linear, indicating that ΔC_p for complex formation is appreciable. This is similar to the well-known observations on

McAuley and Nancollas, J., 1961, 2215.
Nair and Nancollas, J., 1961, 4367.
McAuley and Nancollas, J., 1961, 4458.

dissociation of weak acids. For complex-forming reactions of metals values of ΔC_p have been reported for transition-metal oxalates,⁸ malonates,¹⁰ and succinates.¹¹ Since ΔH varies appreciably with temperature, the variation of $\log_{10} K$ can be represented as a quadratic in T,

$$\log_{10} K = a + bT + cT^2.$$

The values of a, b, and c obtained by the method of least squares from the K values at all



the five temperatures are given in Table 4. The values of K calculated from them are not more than 1.5% different from the observed values.

TABLE 4.

Parameters for temperature-dependence of $\log_{10} K$.

	a	$-10^{2}b$	10 ⁵ c
MnPh	6·365	2.975	5.897
CoPh	5.690	2.374	4.752
NiPh	7.795	3.867	6.912

The thermodynamic functions ΔG , ΔH , ΔC_p , and ΔS for the complex formation were calculated from the relations, $\Delta G = -2.3026 \mathbf{R}T \log_{10} K$, $\Delta H = 2.3026 \mathbf{R}T^2 (b + 2cT)$, $\Delta C_p = 4.6052 \mathbf{R}T (b + 3cT)$, and $\Delta S = (\Delta H - \Delta G)/T$, and are given in Table 5. Un-

TABLE 5.

Thermodynamic functions.

	ΔH	$-\Delta G$	ΔS	ΔC
Reaction	(kcal. mole ⁻¹)	(kcal. mole ⁻¹)	(cal. deg. ⁻¹ mole ⁻¹)	(cal. deg. ⁻¹)
$Mn^{2+} + Ph^{2-} \longrightarrow MnPh$	2.20 + 0.05	3.739 ± 0.006	19.9 ± 0.3	63 ± 20
$Co^{2+} + Ph^{2-} \longrightarrow CoPh$	1.87 ± 0.05	3.860 ± 0.004	19.2 ± 0.2	51 ± 15
$Ni^{2+} + Ph^{2-} \longrightarrow NiPh \dots$	$1.76_{5} \pm 0.05$	4.026 ± 0.005	19.4 ± 0.3	68 ± 20

certainties in the last three quantities were estimated by using different combinations of experimental K values at three temperatures in the experimental range for the calculation of the parameters a, b, and c. ΔC_p is subject to great uncertainties.

 ΔS_{hyd} (MPh) may be obtained from the relation

$$\Delta S_{\rm hyd}(\rm MPh) = \Delta S - \Delta S_{\rm g}(\rm MPh) + \Delta S_{\rm hyd}(\rm M^{2+}) + \Delta S_{\rm hyd}(\rm Ph^{2-}),$$

where ΔS_g and ΔS_{hyd} are the gas and the hydration entropies of the species indicated. ΔS_g was calculated by assuming a planar model for the metal phthalate, and the method of calculation has been described elsewhere.¹² S° for manganese ion is that obtained by Walkley; ¹³ S° for cobalt and nickel ions are those evaluated by Staveley and Randall ¹⁴ (S° values are -18, -22, and -23 cal. deg.⁻¹ mole⁻¹ for Mn²⁺, Co²⁺, and Ni²⁺, respectively). $\Delta S_{hyd}(Ph^{2-})$ was obtained by interpolation on a plot of ΔS_{hyd} of similar bivalent anions against r^{-1} , the latter being calculated from the ionic mobilities of the respective ions by applying Stokes's law. $S^{\circ}(Ph^{2-})$ was obtained as 4.6 cal. deg.⁻¹ mole⁻¹. Table 6 gives the entropy values.

TABLE	6
TUDLE	U

Entropy values (cal. deg.⁻¹ mole⁻¹).

Species	ΔS	$S_{g}(MPh)$	$S^{\circ}(MPh)$	$-\Delta S_{hyd}(MPh)$	r ₊ (Å) 14
	19.9	73.5	6.5	67.0	0.80
	$19 \cdot 2$	73 ·6	1.8	71.8	0.72
	19.4	73 .6	1.0	72.6	0.69
	Species	Species ΔS	$\begin{array}{cccc} {\rm Species} & \Delta S & S_{\rm g}({\rm MPh}) \\ \hline & & 19.9 & 73.5 \\ \hline & & 19.2 & 73.6 \\ \hline & & 19.4 & 73.6 \end{array}$	$\begin{array}{ccccccc} {\rm Species} & \Delta S & S_{\rm g}({\rm MPh}) & S^{\circ}({\rm MPh}) \\ \hline & & 19\cdot9 & 73\cdot5 & 6\cdot5 \\ \hline & & 19\cdot2 & 73\cdot6 & 1\cdot8 \\ \hline & & 19\cdot4 & 73\cdot6 & 1\cdot0 \\ \end{array}$	$\begin{array}{cccccccc} {\rm Species} & \Delta S & S_{\rm g}({\rm MPh}) & S^{\circ}({\rm MPh}) &\Delta S_{\rm hyd}({\rm MPh}) \\ \hline & & 19\cdot9 & 73\cdot5 & 6\cdot5 & 67\cdot0 \\ \hline & & 19\cdot2 & 73\cdot6 & 1\cdot8 & 71\cdot8 \\ \hline & & 19\cdot4 & 73\cdot6 & 1\cdot0 & 72\cdot6 \end{array}$

 ΔS for the formation of the phthalate complex is essentially the same for all the three cations and is found to be of the same order as for their succinates ¹¹ (18—20 cal. deg.⁻¹ mole⁻¹). The enthalpy change ΔH opposes the formation reaction, as was reported for other dicarboxylates. However, this opposition is less for phthalates than for the succinates, thereby leading to a larger $-\Delta G$ value for the phthalate formation. The reaction occurs because of the high entropy gain of the water molecules in the field of the charged ions, resulting from charge neutralisation when the complex is formed. Williams ¹⁵ has suggested that for bivalent cations the heats of hydration, as well as the heats of formation of their complexes, could be represented by an empirical equation combining electrostatic and covalent interaction, together with additional stabilisation due to the different available bonding orbitals of the cations. Thus

 $-\Delta H = A(z/r_{+}) + BI_{02} - C(1/r_{+}^{3})$

where z is the cationic charge, I_{02} the ionisation potential, and A, B, and C are arbitrary constants. When the entropy of formation of a complex is small and the enthalpy term dominant, e.g., with neutral ligands, the stability follows the same order as the enthalpy change for a series of cations forming complexes with the same ligand. With the dicarboxylates, however, the formation reaction is endothermic and the interaction may be mainly electrostatic rather than covalent; ΔH is less unfavourable the smaller the value of r_{+} . $-\Delta S_{hyd}$ (MPh) follows the same trend as r_{+}^{-1} , and is slightly greater than the corresponding term for the succinates ¹¹ (64·4—69·5); this probably indicates less charge neutralisation in the case of the phthalates.

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College of Advanced Technology, Gosta Green, Birmingham, 4.

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¹² Nair and Nancollas, *J.*, 1958, 3706.

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