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ENTHALPY OF COMPLEX FORMATION BY CALORIMETRY: PHTHALATES OF MANGANESE, NICKEL, AND COPPER

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ABSTRACT

Enthalpies of formation of complexes of bivalent manganese, nickel and cupric ions with phthalate ion are determined by direct calorimetry and the results are compared with those derived earlier from temperature coefficient of K values, obtained by precision potentiometry.

INTRODUCTION

Enthalpy data could be obtained either from precise measurements of the equilibrium constant over a wide range of temperature or by direct calorimetry. It has generally been held that direct calorimetry is superior[1] although temperature coefficient measurements are more convenient for obtaining ΔC_p; in a few cases it has been established that ΔH values obtained by temperature coefficient method are as reliable as the calorimetric values[2].

In the present investigation, enthalpies of ion association between manganese and nickel with phthalate ion are determined by direct calorimetry to verify those obtained from temperature coefficient of K values derived from precision potentiometry[3]. Further, enthalpy of association of phthalate ion with the cupric ion is reported.

EXPERIMENTAL

The calorimeter

The calorimeter of the differential type is shown in Fig. 1. It consists of two 300-ml Dewar vessels (V) cemented into polythene containers (C) with close fitting covers. The containers and their lids carry brass flanges which can be screwed together with six thumb screws; water-tight seals are ensured by using O rings or rubber gaskets (G) between the flanges. The lids are firmly cemented to a flat perspex plate supported from the thick lid of the thermostat bath by means of aluminium rods (A). Holes are drilled in the lids to accommodate stirrers (S), thermocouple (T) and supports (H) and (M) for the heating coil and mixing device, respectively. Water-tight seals are made with Araldite epoxy cement. The contents of the calorimeters are stirred with

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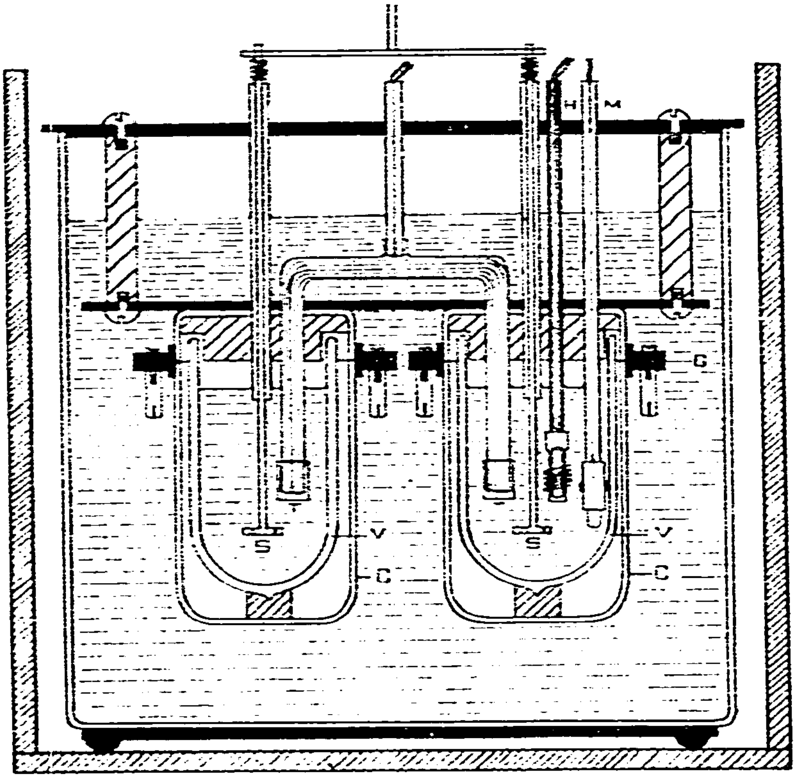

Fig. 1. The calorimeter.

vibrating perspex discs which have conical holes in their faces (Fig. 2B). The stirrer stems (S) pass through close fitting tube supports in the lids. The stems are joined by a horizontal perspex strip attached to a vibrating arm actuated by the stirrer motor of the thermostat bath. Heat effects caused by the moving parts of the conventional rotary stirrers are thus avoided as the maximum vertical movement of the stirrer discs is only about 1/8". The glass solution-mixing device (M) is attached to a supporting tube by a teflon clip cemented to the tube. The mixing device can be closed by means of rubber stoppers cemented to perspex discs (Fig. 2C). Nylon threads, fastened to the discs, are passed up the supporting tube and in an experiment mixing is achieved by pulling these threads.

The thermostat consists of a large glass trough 12" in diameter and 12" in height fitted into a thick wooden box lined with heat-insulating material like felt or thermocole. The heavy perspex circular lid is cut into two halves: one half carrying the bath stirrer, heater, toluene regulator and a thermometer; the other supporting the leads and the control panel (Fig. 2A) of the heating circuit. The temperature is maintained by a small heater of about 25 W rating which is controlled by an electronic relay actuated by a toluene mercury regulator.

Temperature measurements in the calorimeter are very conveniently made by use of multi-junction thermels. The thermel is constructed by using 22 SWG constantan wire and 32 SWG enamelled copper wire. The constantan wire is heated over

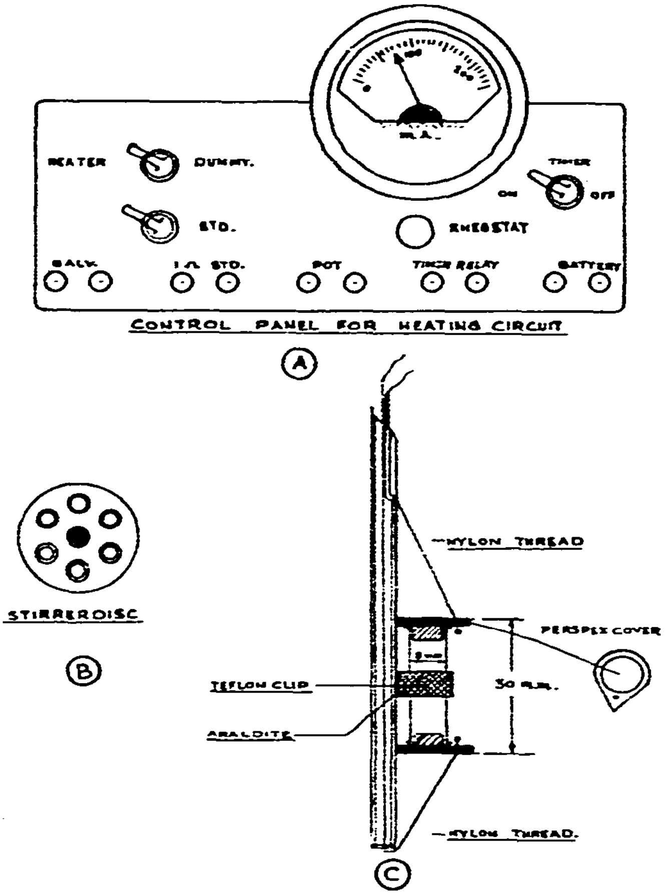

Fig. 2.

a flame and annealed to remove strain and coated with Dr. Beck's epoxy resin. The wire is cut into 10″ lengths and the ends are soldered to enamelled copper wires of equal lengths. Insulation of each individual member of the thermel is ensured by slipping thin polythene sleeves over the pairs of wires. The thermel consists of 19 junctions which are accommodated in a glass U tube with terminal copper leads of 24 SWG enamelled wire being taken out at the apex of the tube. The soldered junction ends are protected by thin glass sleeves filled with melted naphthalene for thermal contact. The leads are soldered to appropriate terminals in the control panel.

The heating coil for calibration is of about 25-Ω resistance and is made by winding non-inductively 36 SWG constantan wire coated with Dr. Beck's epoxy cement, on an open metal frame also coated with the resin. The ends are soldered to 24 SWG enamelled copper wire leads threaded through the supporting glass tube and soldered to appropriate terminals in the control panel. The current from a 6 V accumulator (or a 4.5 V heavy duty dry-cell battery) regulated with a 100-Ω rheostat passes through an 1-Ω standard resistance and either the heater or (when this is out of circuit) a dummy resistor offering identical load. The potential drops across the standard resistance or across a definite part of the heater are measured with a sensitive potentiometer or more conveniently with a Radiometer millivoltmeter Type PH4. The variable resistance and switches used had low contact resistances.

The measurement of time in the calibration experiment is carried out with a stop watch reading to ±0.1 sec and manual operation of the heater switch. The error in synchronising the starting and stopping of the stop watch with the switching on and off of the heater does not exceed 0.5% on the timing of a two minute heating period and as such will not affect the accuracy of the calibration. Thermocouple e.m.f.'s were measured using a high gain DC amplifier, the Keithley nanovoltmeter Model 149 with a Browne Electronic Recorder Model No. Y 143 X (Keithley Instruments Inc.). For some of the experiments, measurements were made with a Leeds and Northrup high sensitivity galvanometer giving a deflection of 1 mm at one meter distance for 0.1 μV, enabling temperature changes of the order of 0.0001 °C to be measured.

PROCEDURE

Heat of solution of KCl

KCl (E. Merck Guaranteed Reagent quality) ground to a fine powder using agate pestle and mortar was dried at 105°C for 2 h and stored in a desiccator over conc. H_2SO_4 for use. The calorimeter containing about 200 g of water in each vessel and the required weight of KCl in the mixing device was allowed to reach equilibrium in the thermostat at 25°C overnight. The stirring was commenced and the heating current stabilised for 2 h under dummy load. Thermocouple e.m.f. readings were taken every minute till a steady rate of change was established. Heating current was then passed for a known time (about 120 sec) measured with a stop watch and the e.m.f. values were noted every minute until a uniform drift was again observed. Mixing was then effected and complete solution was attained within 5 min. After the re-establishment of a linear relationship, further heat was introduced by means of the heating coil. In the experiments done with the Keithley nanovoltmeter the readings of e.m.f. and time were automatically recorded by the recorder.

Heats of complex formation

The metal chloride solution was placed in one of the Dewar vessels and the required weight of "AnalaR" potassium hydrogen phthalate in the solution container. The procedure is as given above.

RESULTS AND DISCUSSION

Evaluation of the water equivalent in cal/uv and of the heat changes were made using the method of Eitel[4]. The heat changes are sub-divided into three parts corresponding to the fore and after periods (a) and (r) and to the variation during the change itself (x). The first temperature reading θ_0 is at time t_0 and mixing is effected at time t_i at which the temperature is θ_i. The rate of change in the fore period $v_a = (\theta_0 - \theta_i)/(t_i - t_0)$ and the average temperature $\theta_a = \frac{1}{2}(\theta_0 + \theta_i)$. The heat change is given by the change in the reading from θ_i to θ_e. The θ_e marks the after-rating period and θ_i its termination and the corresponding times being t_e and t_i. The rate of change and average temperature in this period are respectively

$$\frac{(\theta_e-\theta_1)}{(t_1-t_e)} = v_r \text{ and } \theta_r = \tfrac{1}{2}(\theta_e+\theta_1)$$

The corrected temperature change is given by the Regnault–Pfaundler formula:

$$\Delta\theta' = \theta_e-\theta_1+(t_e-t_i)\,v_a+\frac{(v_r-v_a)}{(\theta_r-\theta_a)}\left[\tfrac{1}{2}(\theta_e+\theta_i)+\sum_{i}^{t_e-t_i-1}-(t_e-t_i)\,\theta_a\right]$$

Fore and after periods were usually about 6 to 10 min each.

Heat of solution of KCl to a dilution of 1:18000 at 25°C is given in Table I. The mean heat of solution to a dilution of 1 in 18 000 was 4.154 kcal/mole which is in fair agreement with the literature values[5], considering the criticisms of Sunner and Wadso[6] of the use of KCl as a calorimetric reference.

Determinations of the heats of complex formation were made by using the method of Anderson, Malcolm, and Parton. The temperature changes on dilution of potassium hydrogen phthalate with metal chloride solution and with a KCl solution of the same ionic strength were measured. It was assumed that the difference was due to the formation of the complex. By taking a higher proportion of M^{2+}: phthalate, species such as $M[C_6H_4(CO_2)_2]^{2-}$ can be avoided and the study limited to 1:1 species.

TABLE I

HEAT OF SOLUTION OF KCl

	Expt. 1	*Expt. 2*
Weight of KCl (g)	0.1258	0.0470
Weight of water (g)	203.98	193.19
E (V)	2.5538	1.3001
E_s (V)	0.1482	0.0750
t (sec)	179.8	120.0
Corr. (divisions)	17.5	115
Corr. (for KCl dilution)	7.5	107
Dilution	1:7400	1:18 000
Heat absorbed (kcal/mole)	4.135	4.154

The pH of the solution was measured at the end of each experiment, by means of cell: glass electrode |solution under study| sat. KCl, calomel. From the equations for the total metal ion and the potassium acid phthalate concentrations, T_M and T_A, the concentration of the complex species is calculated. The association constants obtained are seen to be in good agreement with the values reported in the literature. The activity coefficients were calculated from the Davies equation[7]

$$\log f_z = Az^2\left(\frac{I^{1/2}}{1+I^{1/2}}-0.2\,I\right)$$

The results are tabulated in Table II in which Q_{corr} is the corrected heat absorbed in each experiment and ΔH_i the heat change per mole of complex. Fig. 3 shows the e.m.f.–time plot in a typical run. Heat effects due to the opening of the capsule was never more than 0.1 cal. The heats of association at $I = 0$ (ΔH^0) are related to the observed ΔH_i by

$$\Delta H_i = \Delta H^0 - 3\,RT^2\left(\frac{1}{D}\cdot\frac{dT}{dD} + \frac{1}{T}\right)\ln f_2$$

where f_2 is the activity coefficient of a bivalent ion[8]. The value of D the solvent dielectric constant and its temperature dependence were those of Akerlof[9]. ΔH^0

TABLE II

ENTHALPIES OF FORMATION OF PHTHALATES

$T_A \times 10^3$ (moles)	$T_M \times 10^3$ (moles)	$I \times 10^3$ (moles)	pH	$[HPh] \times 10^3$ (moles)	$[MPh] \times 10^3$ (moles)	Q_{corr} (cal)	ΔH (kcal·mole^{-1})
Copper phthalate							
9.5348	9.9730	33.20	3.398	5.665	2.080	3.3	1.58
9.5348	10.1946	33.78	3.402	5.676	2.079	3.2	1.54
						Av.: ΔH =	1.56 ± 0.02
Nickel phthalate							
4.8272	7.9631	27.99	3.880	3.895	0.355	0.5	1.40
7.8699	7.2031	28.00	3.864	7.713	0.501	0.7	1.39
7.6567	6.7915	27.07	3.865	6.264	0.471	0.7	1.47
						Av.: ΔH =	1.42 ± 0.05
Manganese phthalate							
6.9627	5.3372	22.44	3.970	5.872	0.274	0.6	2.18
7.4602	5.8521	24.50	3.959	6.278	0.287	0.6	2.09
						Av.: ΔH =	2.13 ± 0.05

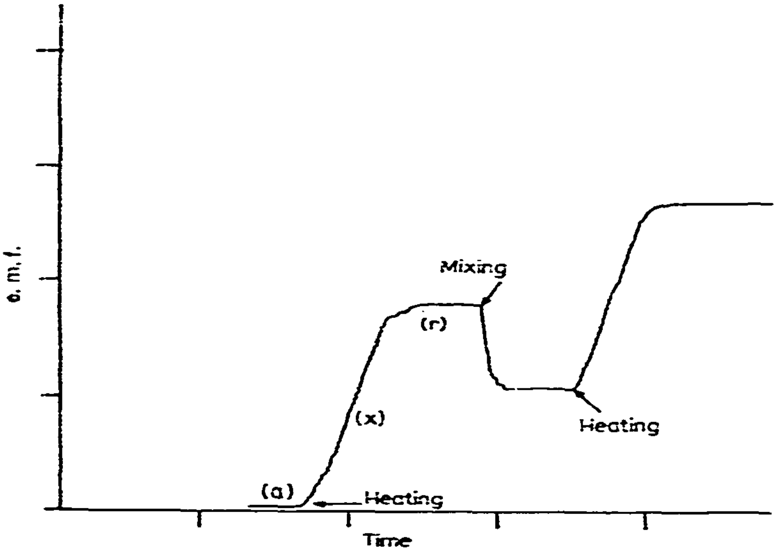

Fig. 3. Heat of solution of KCl.

values are given in Table III and the agreement with those obtained from temperature coefficient data is good in the case of both manganese and nickel phthalates.

TABLE III

IONIC STRENGTH CORRECTIONS

$I \times 10^2$ (*moles*)	ΔH_i (*kcal·mole*$^{-1}$)	ΔH^0 (*kcal·mole*$^{-1}$)
Copper phthalate		
3.320	1.58	2.03
3.378	1.54	1.99
		Av.: ΔH^0 = 2.01
Nickel phthalate		
2.799	1.40	1.83
2.800	1.39	1.82
2.707	1.47	1.90
		Av.: ΔH^0 = 1.88
Manganese phthalate		
2.214	2.18	2.58
2.450	2.09	2.50
		Av.: ΔH^0 = 2.54

The values of ΔS^0 from the new ΔH^0 are ΔS^0(NiPh) = 19.8 cal·deg^{-1}·mole^{-1} a change of only 1.2 cal·deg^{-1}·mole^{-1}. It would seem that use of sufficiently large temperature range yields ΔH^0 values which are more reliable than is usually supposed. This view is substantiated by recent work in solution calorimetry.

The thermodynamic data for copper phthalate, along with those of manganese, cobalt, nickel and zinc obtained from temperature coefficient measurements by Nair[3], are presented in Table IV. ΔS_{hyd}(CuPh) has been obtained following the same procedure as described by Nair.

TABLE IV

ENTROPY OF HYDRATION OF M Ph FOR PHTHALATES

	Mn[a]	*Co*[a]	*Ni*[a]	*Cu*	*Zn*[a]
$\log_{10} K^{298}$ (M Ph)	2.741	2.831	2.952	4.038[b]	2.893
ΔG^0	3.739	3.860	4.026	5.51	3.95
ΔH^0	2.20	1.87	1.76	2.01	3.16
ΔS^0	19.9	19.2	19.4	25.2	23.8
S_g (M Ph)	73.5	73.6	73.6	73.7	73.7
ΔS_{hyd} (M Ph)	67.0	71.8	72.6	67.5	70.75
r_+ (Å)	0.80	0.72	0.69	0.70	0.74

[a] Values of Nair. [b] The value of $\log_{10} K^{298}$ obtained in this work are seen to be in excellent agreement with those of Peacock and James, and Yasuda *et al.*

For essentially electrostatic interactions, such as those involving oxygen coordinating anionic ligands, endothermic heat changes are observed, since the coulombic forces will vary with temperature in the same way as the macroscopic dielectric constant of water. In spite of this unfavourable enthalpy change, the complexes are stabilised by the relatively large positive entropy changes reflecting the liberation of coordinated water molecules from the interacting ions as a result of partial or complete neutralisation of charge. The crystal fields produced by oxygen coordinating ligands are quite similar to those of the water molecules; therefore ΔH will not be influenced considerably by ligand-field stabilisation. To explain the abnormally large endothermic heat changes accompanying the formation of the copper–monomalonate and copper–monosuccinate complexes, it has been suggested[10] that the d^9 electronic configuration of the copper(II) is capable of additional stabilisation due to tetragonal distortion of the octahedral symmetry as a result of the Jahn–Teller effect resulting in four short bonds in the xy-plane and two long bonds along the z-axis. In keeping with the large positive entropy of formation, it has been suggested that the closer contact of the metal and ligand donor atoms in the xy plane will result in a more effective charge neutralisation in the comples. At the limit of distortion, a change of coordination from six in the aquo-ion to four in the complex will also lead to an increased positive ΔS, but in this additional endothermicity will be involved in the breaking of the metal–water bonds. In the case of phthalates, although there is a significant entropy change accompanying the complex formation in the case of copper(II), there is somewhat less pronounced endothermicity, suggesting that relatively there is greater covalency in the bonding involved in comparison with succinates[11].

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