182. *Thermodynamics of Ion Association. Part X.[1] Calorimetric Heats of Formation.*

By A. McAuley and G. H. Nancollas.

A sensitive calorimeter for the determination of heats of ion-pair formation in solution has been constructed and tested. The heats of association of Mn^{2+} and Co^{2+} ions with malonate ion have been measured and are compared with those obtained from the temperature dependence of the association constants.

THE degree of association of ions in an electrolyte solution has largely been studied at a single temperature. Although this provides values for the free energy of ion-pair formation, no information is obtained concerning ΔH and ΔS. In some cases where a number of temperatures have been studied, ΔH values of varying reliability have been obtained. In such work it is important to cover as wide a range of temperature as possible in order to minimise extrapolation errors. However, these results must still be used with caution, and the most reliable values of heats of formation are those obtained by direct calorimetry.[2,3]

Since, for transition-metal ions, ligand field and other effects produce contributions to ΔH, it is important to obtain accurate values. Owing to the lack of such data, many workers have used ΔG in place of ΔH, thereby implying a constant ΔS.

A sensitive calorimeter has been contructed, and calibrated by determining the heat of solution of potassium chloride. In order to compare ΔH values obtained calorimetrically

[1] Part IX, McAuley and Nancollas, *J.*, 1961, 4458.
[2] Davies, Singer, and Staveley, *J.*, 1954, 2304.
[3] Ciampolini, Paoletti, and Sacconi, *J.*, 1960, 4553.

and from temperature-dependence data, measurements have been made with manganese and cobalt malonates. For these systems, a precise e.m.f. method was used previously over a 45° temperature range.[4]

<div align="center">EXPERIMENTAL</div>

The Calorimeter.—The calorimeter, of the differential type, is shown in Fig. 1. It consists of two 1·5 l. Dewar vessels (A) cemented into brass containers (B) fitted with flanges on which flat brass lids could be screwed with six thumb screws; watertight seals were ensured by using ◯-rings (C). In order to limit vapour spaces inside the calorimeter, Perspex discs (D) were cemented to the undersides of the brass lids. Holes were bored in the lids to accommodate the stirrers (E), supports (F and G) for the heating coil and solution container, respectively, and B24 Quickfit sockets for the thermopile (H). Watertight seals were made with Araldite cement and the whole calorimeter was supported on a central brass pillar and clamped in a thermostat maintained at 25° ± 0·01° with the water level as indicated.

The vibratory disc stirrers passed through rubber diaphragms (I) and were attached by means of dual chucks to a central vibratory motor (Shandon Scientific Co.) through (J). In this way, heat effects caused by the moving parts of rotary stirrers were avoided as the maximum vertical movement of the stirrer discs was only 1/16 in. The solution container (K) was made from a B24 Quickfit air-bleed ground flat at each end on to which 1/8 in. thick Perspex discs could be sealed with silicone grease. This mixing device fitted into a B24 socket cemented to a Perspex former (L) which was attached to a supporting glass rod and tube (G). Nylon threads fastened to the two Perspec discs passed up this tube and, in an experiment, mixing was achieved by pulling these threads.

The thermopile (H) consisted of 60 junctions of 20 s.w.g. constantin wire (Vactite Wire Co., thermocouple grade Eureka, 0·99 ohm/yard) and 34 s.w.g. enamelled copper wire bound together with Nylon thread. The constantan was covered with 1-mm. Polythene sleeving, and the junctions were made with soft solder. They were insulated with Araldite cement and arranged so as to be at about 1/8 in. intervals over a 4 in. depth of solution in each Dewar vessel.[5] The parts of the thermopile outside the Dewar vessels were contained in 1 in. diameter rubber tubing with B24 cones sealed to its ends.

The heating coil (M), of resistance 19·307 ohms, was made by winding nichrome wire (32 s.w.g.) on a glass former. The ends were welded to platinum loops sealed into the glass support (F), and connections were made with copper leads soldered to the platinum. The heating circuit was similar to that of Pitzer.[6] Current from a 12 v battery, regulated with a 250 ohm potentiometer, passed through a 1 ohm standard resistance and either the heater or, when this was out of circuit, a substitute resistance offering an identical load. The potential drop across the standard resistance was measured with a Tinsley potentiometer.

Thermocouple e.m.f.s were obtained by using a Pye precision decade potentiometer (type 7600) in conjunction with a Scalamp galvanometer (type 7904/S) and galvanometer pre-amplifier (type 11330). Discrimination was better than 0·1 μv, corresponding to a heat change of about 0·1 cal. By means of a switch incorporated in the potentiometer it was possible to reverse all circuit polarities in order to eliminate spurious e.m.f.s; these were in all cases negligible.

Heat of Solution of Potassium Chloride.—The calorimeter, containing about 1200 g. of water in each vessel and the required weight of potassium chloride in the mixing device, was allowed to reach equilibrium in the thermostat overnight. Stirring was commenced and the heating current was stabilised for 2 hr. under dummy load. Thermocouple e.m.f. readings were then taken every minute until a steady rate of change (0·5—1·0 μv/min.) was established. Heating current was then passed for a known time (about 120 sec.), measured with a 1/10th sec. stop watch, and e.m.f. values were noted each minute until a steady drift was again observed. Mixing was then effected and complete solution was attained within 3—5 min. After the re-establishment of a linear e.m.f.–time relationship, further heat was introduced by means of the heating coil.

Heats of Complex Formation.—Solutions of sodium malonate which had been recrystallised

⁴ Nair and Nancollas, *J.*, 1961, 4367.
⁵ Meares, *Trans. Faraday Soc.*, 1949, **45**, 1066.
⁶ Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.

from distilled water and of " AnalaR " metal chlorides were analysed for cation on an ion-exchange column of Amberlite IR-120 (H^+ form). Metal chloride solution was placed in one of the Dewar vessels, and a solution of sodium malonate in the solution container. In these experiments complete mixing of the contents was obtained within 15 sec.; otherwise the procedure was as given above.

Results and Discussion

Evaluations of water equivalents in cal. μv^{-1} and of the heat changes were made by using Eitel's method.[7] The heat changes were sub-divided into three parts, (a) and (r) corresponding to the e.m.f.–time relationship in the fore- and after-periods, and (x) to the variation during the change itself. The first temperature reading θ_0 (in μv) was at time t_0, and mixing was effected at time t_i at which the temperature was θ_i. The cooling rate in the fore-period was $v_a = (\theta_0 - \theta_i)/(t_i - t_0)$ and the average temperature $\theta_a = \frac{1}{2}(\theta_0 + \theta_i)$. The heat change was given by a rise in e.m.f. from θ_i to θ_e. θ_e marked the start of the after-rating period and θ_l its termination, the corresponding times being t_e and t_l. The rate of cooling and average temperature in this period were respectively $(\theta_e - \theta_l)/(t_l - t_e) = v_x$, and $\theta_r = \frac{1}{2}(\theta_e + \theta_l)$. The corrected temperature change was given by the Regnault–Pfaundler formula,

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

Fore- and after-periods were usually about 6 min. but for the experiments with potassium chloride these were extended to about 10 min.

Many values are given in the literature for the heat of solution of potassium chloride but they refer to a variety of concentrations.[8] Staveley *et al.*,[2] however, has corrected some of the data to a single dilution of 1 mole of potassium chloride in 167 moles of water, and similar corrections have been made in the present work. The heat of solution under these conditions was 4.16 ± 0.03 kcal. mole^{-1} which may be compared with 4.184 ± 0.008 kcal. mole^{-1}.[2] The agreement is reasonable in view of the criticisms by Sunner and Wadsö [9] of the use of potassium chloride as a calorimetric reference.

Determinations of the heats of complex formation were made by using the method of Anderson, Malcolm, and Parton.[10] The temperature changes on dilution of sodium malonate (Na_2A) with metal chloride (MCl_2) solution and with a potassium chloride solution of the same ionic strength were measured. It was assumed that the difference was due to the formation of a complex. Conditions were arranged such that only one such species, MA, was present, and concentrations were calculated by using equations for: total metal ion, $T_m = [M^{2+}] + [MA]$, and total malonic acid, $T_A = [MA] + [A^{2-}]$. Since the pH of the solutions was 6·8—6·9, $[H_2A]$ and $[HA^-]$ were negligible as were corrections for $[MOH^+]$. The association constants $K = \{MA\}/\{M^{2+}\}\{A^{2-}\}$ were those of Nair and Nancollas [4] and activity coefficients were obtained from [11]

$$\log f_z = -Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.2I].$$

The results are given in Table 1 in which $\Delta Q_{(corr.)}$ is the corrected heat absorbed in each experiment and ΔH_i the heat change per mole of complex. Fig. 2 shows the e.m.f.–time plot in a typical run. Heat effects due to the opening of the capsule, studied in blank experiments, were never more than 0·2 cal.

[7] Eitel, " Thermochemical Methods in Silicate Investigation," Rutgers Univ. Press, New Jersey, 1952.
[8] Bichowsky and Rossini, " The Thermochemistry of Chemical Substances," Reinhold, New York, 1936.
[9] Sunner and Wadsö, *Acta Chem. Scand.*, 1959, **13**, 97.
[10] Anderson, Malcolm, and Parton, *J. Phys. Chem.*, 1960, **64**, 494.
[11] Davies, *J.*, 1938, 2093.

The heats of association at $I = 0$, $\Delta H°$, are related to the observed ΔH_i by

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

where f_2 is the activity coefficient of a bivalent ion.   The values of D, the solvent dielectric constant, and its temperature dependence were those of Akerlof.[12] $\Delta H°$ values are given
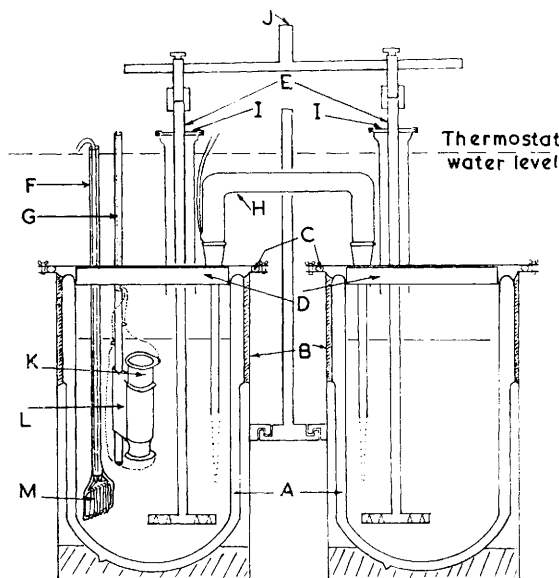

FIG. 1.   The calorimeter with fittings.
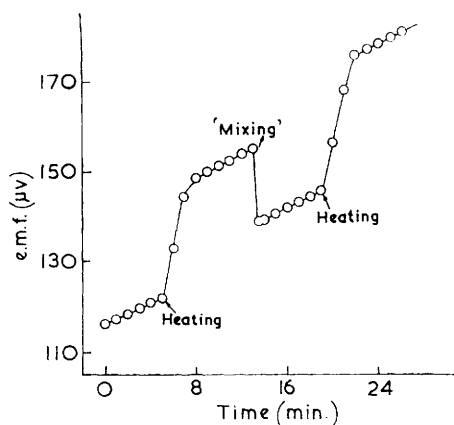

FIG. 2.   A typical e.m.f.–time plot.

TABLE 1.

Heats of complex formation at 25°.

$T_m \times 10^3$ (moles l.$^{-1}$)	$T_A \times 10^3$ (moles l.$^{-1}$)	$I \times 10^3$ (moles l.$^{-1}$)	[MA] $\times 10^3$ (moles l.$^{-1}$)	$\Delta\theta^1$ (μv)	ΔQ (corr.) (cal.)	ΔH_i (kcal. mole^{-1})
			Cobalt malonate			
9·021	4·805	24·28	4·274	11·7$_5$	10·8$_3$	2·53
8·972	4·778	24·20	4·248	10·9$_5$	9·9$_0$	2·33
5·069	5·709	16·37	3·960	11·4$_0$	10·3$_7$	2·62
5·065	6·587	18·33	4·174	12·0$_0$	10·7$_9$	2·59
				Av. $\Delta H_i = 2·52 \pm 0·09$ kcal. mole^{-1}		
			Manganese malonate			
10·198	6·593	30·78	4·820	17·1	15·6$_6$	3·25
11·432	6·643	34·22	5·008	16·7	14·6$_1$	2·92
11·393	8·858	35·75	6·182	26·4	20·3$_6$	3·29
10·222	8·858	33·64	5·956	16·8	19·2$_7$	3·24
11·373	5·715	33·32	4·406	16·8	15·1$_3$	3·43
				Av. $\Delta H_i = 3·23 \pm 0·12$ kcal. mole^{-1}		

in Table 2, and the agreement with those obtained from temperature coefficient data, $\Delta H°$(CoA) = 2·57 kcal. mole^{-1} and $\Delta H°$(MnA) = 3·53 kcal. mole^{-1}, is surprisingly good. The values of $\Delta S°$ from the new $\Delta H°$'s are $\Delta S°$ (CoA) = 26·9 cal. deg.$^{-1}$ mole^{-1} and $\Delta S°$ (MnA) = 27·4 cal. deg.$^{-1}$ mole^{-1} a change of only about 1 cal. deg.$^{-1}$ mole^{-1}.

It would seem, therefore, that the use of a sufficiently large temperature range yields $\Delta H°$ values which are more reliable than was previously supposed.   This view is

[12] Akerlof, *J. Amer. Chem. Soc.*, 1932, **54**, 4130.

TABLE 2.

Ionic strength corrections.

	Cobalt malonate			Manganese malonate	
$I \times 10^2$ (moles l.$^{-1}$)	ΔH_i (kcal. mole^{-1})	ΔH° (kcal. mole^{-1})	$I \times 10^2$ (moles l.$^{-1}$)	ΔH_i (kcal. mole^{-1})	ΔH° (kcal. mole^{-1})
2·428	2·53	2·95	3·078	3·25	3·69
2·420	2·33	2·73	3·422	2·92	3·38
1·637	2·62	2·95	3·575	3·29	3·76
1·833	2·59	2·95	3·364	3·24	3·70
			3·332	3·43	3·88

Av. $\Delta H^\circ = 2\cdot90 \pm 0\cdot08$ kcal. mole^{-1} Av. $\Delta H^\circ = 3\cdot68 \pm 0\cdot12$ kcal. mole^{-1}

substantiated by recent work of Austin and Mair,[13] who have found a calorimetric heat of formation of the bisulphate ion, $\Delta H^\circ = 5\cdot75 \pm 0\cdot20$ kcal. mole^{-1}, in close agreement with 5·60 kcal. mole^{-1} from the temperature dependence of the association constant.[14]

[13] Austin and Mair, *J. Phys. Chem.*, 1962, **66**, 519.
[14] Nair and Nancollas, *J.*, 1958, 4144.