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THE ENTHALPY OF SOLUTION OF PHOSPHOROUS ACID (H_3PO_3) IN WATER

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ABSTRACT

The enthalpies of solution and dilution of H_3PO_3(cryst.) in water at 298.15 K were determined by isoperibol calorimetry. The enthalpy of solution at infinite dilution was -6.3 ± 0.6 kJ mol^{-1}.

INTRODUCTION

The heat of solution of phosphorous acid (H_3PO_3, m.p. 73–74°C) in water is not well-established. A recent compilation [1] of thermodynamic data quotes -0.4 kJ mol^{-1}. A literature report [2] of the determination of the heat of formation of crystalline H_3PO_3 mentions en passant that the heat of solution is small (ca. -1.2 kJ mol^{-1}). Data given in an NBS Circular [3] suggest that the solution process is athermal; the origin of these data is early work by Thomsen [4]. A translation [5] of Thomsen's work quotes $+0.5$ kJ mol^{-1} for the heat of solution. Thomsen's sign convention is the opposite to that currently in use, and it is possible that the result in ref. 1 is a mistranscription of Thomsen's value. This note reports enthalpies of solution in water at 298.15 K to give final solutions in the concentration range 0.01 to 0.06 M.

EXPERIMENTAL

Materials

Two separate batches of phosphorous acid were used, identified as A and B. Batch A was synthesised by the controlled hydrolysis of PCl_3 dissolved in

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TABLE 1

Analytical results

	H_3PO_3	
	Batch A	Batch B
Acidimetric assay	99.6%	99.4%
Reductiometric assay	99.5%	99.6%

CCl_4 according to the procedure of Voigt and Gallais [6]. Batch B was a commercial sample (BDH Ltd.), which was recrystallised three times from water, then evacuated at 0.01 mmHg for several days at room temperature to remove the last traces of water. The most likely active impurity in H_3PO_3 is H_3PO_4, and it is important to assess this quantitatively as the heat of solution of H_3PO_4 is about ten times the corresponding value for H_3PO_3. The ionization constants for H_3PO_3 (pK 2.0 and 6.6) and H_3PO_4 (pK 2.1, 7.2 and 12.7) are similar, so acidimetric assay does not resolve these two acids. Accordingly, both batches were analysed both for total acid and reductiometrically, i.e. by digestion with standard iodine solution overnight at room temperature followed by titration of the excess iodine with standard thiosulphate (Table 1).

In view of the close coincidence of these analytical data, it was assumed that the level of H_3PO_4 contamination in both batches was nil, and the remaining impurity (0.4–0.5%) was inert (probably water; the pure material is very hygroscopic [5]). Samples were stored and handled subsequently in a nitrogen-filled drybox.

Calorimeters

For batch A a commercial LKB Precision Calorimeter System 8700-1 operated in the isoperibol mode at 298.15 K was used. The out-of-balance bridge signal was displayed on a chart recorder, and the system was tested by measuring the enthalpy of neutralization of tris[(hydroxymethyl)amino] methane (THAM) in an excess of 0.1 M HCl, for which $\Delta H(298.15\ \text{K}, 1280 < N < 1464) = -29.72 \pm 0.03$ kJ mol^{-1}. Prosen and Kilday [7] obtain $\Delta H\ (298.15\ \text{K}, N = 1345) = -29.77 \pm 0.03$ kJ mol^{-1} for the same reaction; N is the molar ratio of water to THAM and the uncertainty interval is $\pm 2\bar{s}$, $\bar{s}$ being the standard deviation of the mean.

For batch B, a purpose-built twin solution calorimeter was used operating in the isoperibol mode at 298.15 K [8]. THAM neutralization (see above) was used to test the calorimeter and the ΔH value (298.15 K, $2300 < N < 3700$) was -29.7 ± 0.3 kJ mol^{-1}; this is in satisfactory agreement with the literature value given above.

TABLE 2

Masses of phosphorous acid and enthalpy changes for reaction (1) at 298.15 K

Batch	m [a] (g)	n	$-\Delta H$ [b] (kJ mol^{-1})
A	0.47672	955	1.53
A	0.37854	1203	2.01
A	0.35498	1288	2.12
B	0.33109	1376	2.59
A	0.29517	1543	2.54
A	0.28329	1607	2.62
B	0.25779	1766	2.62
B	0.24726	1842	2.85
B	0.13170	3458	3.54
A	0.10818	4210	4.32

[a] Mass in vacuo; density = 1.651 g cm^{-3} [5].

[b] Corrected for 0.5 mass % of inert impurity (see Experimental section).

RESULTS AND DISCUSSION

Nine separate determinations of the heat of solution of H_3PO_3 were made using 100 cm^3 of deoxygenated water as the calorimeter charge

$$H_3PO_3(\text{cryst.}) + nH_2O(l) = H_3PO_3 \cdot nH_2O(\text{solution}) \quad (1)$$

The results in Table 2 regress satisfactorily ($r^2 = 0.95$) to give eqn. (2)

$$-\Delta H = (6.35 \pm 0.29) - (149 \pm 11)/n^{1/2} \quad (2)$$

In eqn. (2) the uncertainty intervals are single standard deviations of the regression coefficients. At infinite dilution ($n \to \infty$), the equation indicates that the enthalpy of solution of crystalline H_3PO_3 is -6.3 ± 0.6 kJ mol^{-1} at 298.15 K.

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