Thermochimica Acta, 194 (1992) 117–127
Elsevier Science Publishers B.V., Amsterdam

The standard enthalpies of formation of zinc orthophosphate and its hydrates

Hussein M.A. Al-Maydama, Peter J. Gardner and Iain W. McAra

Department of Chemistry, Royal Holloway and Bedford New College, Egham Hill, Egham, Surrey TW20 0EX (UK)

(Received 8 April 1991)

Abstract

The standard enthalpies of formation at 298.15 K of $Zn_3(PO_4)_2$(c), $Zn_3(PO_4)_2 2H_2O$(c) and $Zn_3(PO_4)_2 4H_2O$(c) were determined as -2891.2 ± 3.3, -3492.1 ± 3.3 and -4093.5 ± 3.3 kJ mol^{-1}, respectively, by isoperibol solution-reaction calorimetry. Some thermodynamic information concerning a tetrahydrate polymorph is also presented and the kinetic results for the rate of hydration of the anhydrate in liquid water are discussed.

INTRODUCTION

Zinc orthophosphate $Zn_3(PO_4)_2$ forms two well defined hydrates; a dihydrate and tetrahydrate [1–3]. The crystal structures of these materials are well established [4–9] but evidence for hydrates of other stoichiometries, for example a monohydrate, is less sound [10]. Zinc orthophosphate dihydrate is a widely used corrosion inhibitor in the formulation of marine paints [11,12]. As part of a programme to investigate the mechanism of the corrosion inhibition of this material, we have determined the enthalpy of formation of the anhydrate, the dihydrate and the tetrahydrate as well as studying the rate of interconversion of these forms under well defined conditions. There is an extensive literature on the existence of polymorphic forms of the anhydrate [6–9] and of the hydrates [4,5,13] and we have determined the enthalpy of formation of a tetrahydrate polymorph. The experimental procedures used were isoperibol solution-reaction calorimetry and batch microcalorimetry.

EXPERIMENTAL

Materials

The anhydrous zinc phosphate and the hydrates were prepared by a modification of an unpublished procedure of Bishop [14]. The general philosophy of the method is to use extremely pure starting materials, thus eliminating the necessity for extensive purification of the products. Zinc oxide (BDH, AnalaR, 165 g) was slurried in deionised water (1500 cm^3) at room temperature for 30 minutes using a high-speed Silverson stirrer. Efficient mixing was very important as one of the reactants and the product are solids. Orthophosphoric acid (BDH, AnalaR, 85% aqueous solution, 168 g) was added dropwise over approximately 30 minutes with continuous stirring, maintaining the mixture temperature below 70°C. The above quantities represent a 5 mol.% excess of acid relative to ZnO. The product was filtered at the pump and washed with deionised water until the pH of the wash water was in excess of 6. About 50 g of the crude product was distributed as a shallow bed in a stainless steel tray and heated in air to 60°C, with occasional agitation, for 3 days to yield $Zn_3(PO_4)_2 4H_2O$. A further batch of about 50 g was treated at 115°C for 24 hours to give $Zn_3(PO_4)_2 2H_2O$. The final batch, about 50 g, was heated to 550°C for 5 hours to give $Zn_3(PO_4)_2$.

By analysing the products for both zinc and phosphate, Bishop [14] has established that this synthetic procedure yields orthophosphate only and that acid phosphates are absent. Our analytical procedure, based on gravimetric dehydration (550°C for 5 h) to the anhydrate, is recommended in British Standard 5193 [15]. Two separate batches of tetrahydrate were prepared (identified as **I** and **II**) and the analytical results are collected in Table 1. In addition, the X-ray powder patterns agreed with those of authentic samples [16]; in particular, the absence of residual ZnO in the samples was established. The different polymorphs of the tetrahydrate (see the Results and Discussion section below) are not distinguishable by XRD but may be by thermal analysis. The material synthesised here loses water in two distinct steps; 2 moles between 72 and 104°C, and a further 2 moles between 285 and 308°C. This is characteristic behaviour of the α-hopeite form.

TABLE 1

Composition of zinc orthophosphates (n in $Zn_3(PO_4)_2 nH_2O$) from gravimetric dehydration [15] [a]

Nominal formula	n [b]
$Zn_3(PO_4)_2$	0.024
$Zn_3(PO_4)_2 2H_2O$	1.99
$Zn_3(PO_4)_2 4H_2O$ (**I**)	3.94
$Zn_3(PO_4)_2 4H_2O$ (**II**)	3.97

[a] Repeat analyses of the stock materials after calorimetric measurements were complete gave identical results.

[b] The accuracy of these analyses is ±0.02.

Zinc oxide (BDH, AnalaR, Batch number 324528/11) contained residual carbonate (0.25 mass%) and several metallic impurities between 2 and 50 ppm. It was pre-treated at 600°C for 4 h to destroy the residual carbonate.

Orthophosphoric acid (BDH, AnalaR) was diluted with deionised water to give a stock solution for calorimetry of about 7.5 mass %; potentiometric titration established the concentration as 0.795 M (or $H_3PO_4 69.8H_2O$).

Calorimeters

A purpose-built twin-solution calorimeter (100 cm^3) operating in the isoperibol mode at 298.15 K was used for the solution-reaction calorimetry [17]. The system was tested by measuring the enthalpy of neutralisation of tris(hydroxymethylamino)methane (THAM) in an excess of 0.1 M HCl solution as $\Delta H(298.15\ K,\ 1790 < N < 2150) = -29.79 \pm 0.03$ kJ mol^{-1}. Prosen and Kilday [18] obtained a value of $\Delta H(298.15\ K,\ N = 1345) = -29.88 \pm 0.03$ kJ mol^{-1} for the same reaction; N is the mole ratio of water to THAM and the uncertainty interval is $\pm 2s$, s being the standard deviation of the mean.

A commercial sorption microcalorimeter (LKB Model 2107-030) operating at 298.15 K in the batch mode was used for the interconversion studies. The system was tested with the THAM neutralisation reaction described above. For eight experiments, $\Delta H(298.15\ K) = -28.5 \pm 2.7$ kJ mol^{-1}. Sample masses in the phosphate experiments were between 7 and 60 mg and the blank correction (arising from the frictional effect of the water (0.5 g) filling the cell) was approximately 100 mJ, about 10% of the total thermal output with the lower reactant masses.

For thermogravimetric analysis (TGA), a Perkin–Elmer Model TGS-2 was used with a nitrogen purge gas flowing at 40 cm^3 min^{-1} and a temperature ramp rate of 5 K min^{-1}.

RESULTS AND DISCUSSION

Reaction calorimetry

Zinc phosphate has a vanishingly small aqueous solubility [19] at near neutral pH ($K_{sp} \approx 10^{-35}$ at 298.15 K and pH ≈ 4) but the solubility rises sharply at higher or lower pH [20]. Preliminary experiments under calorimetric conditions showed that the lowest concentration of aqueous H_3PO_4 for the rapid dissolution (≤ 2 min) of 0.1 g ZnO in $H_3PO_4(aq)$ was about 0.8 M; the zinc phosphates all dissolved in less than 1 minute at this molarity. The species present in the final solution were not identified. Certainly Zn^{2+} and PO_4^{3-} were present, and possibly $ZnHPO_4$ and $ZnH_2PO_4^+$ were present in addition [19]. However, by careful choice of

TABLE 2

Enthalpies of reaction of ZnO(c) with excess aqueous H_3PO_4 [a] at 298.15 K (eqn. (1))

Mass [b] ZnO (g)	Mole ratio ($H_2O:Zn^{2+}$)	$-\Delta H$ (kJ mol^{-1})
0.03606	12527	93.05
0.05321	8489	92.55
0.06995	6458	92.97
0.07357	6140	92.55
0.08365	5400	92.72
0.08575	5268	93.13
0.10131	4459	92.97
0.11355	3985	92.59
0.11791	3831	93.18
0.14801	3052	93.10
0.18107	2495	93.20
0.19472	2324	93.12
	$\langle -\Delta H \rangle \pm 2(\text{sdm}) = 92.93 \pm 0.15$ kJ mol^{-1}	

[a] The initial concentration of the H_3PO_4 was 0.795 M or $H_3PO_4 69.8H_2O$, i.e. $m/(n+2) = 69.8$ in eqn. (1).

[b] Mass in vacuo, $\rho(ZnO) = 5.68$ g cm^{-3} [1].

concentration, it may be assumed that the same (but unidentified) final thermodynamic state is formed in both the ZnO + H_3PO_4(aq) experiments and the zinc phosphate + H_3PO_4(aq) experiments and, consequently, its thermodynamic identity is not significant in deriving the heats of formation of zinc phosphate. In the equations that follow, the final thermodynamic state is nominally identified as containing Zn^{2+} and PO_4^{3-} only.

The enthalpy of reaction of ZnO with H_3PO_4(aq) was measured using a range of initial masses of ZnO so that the molar ratio of H_2O to Zn^{2+} in the final solution varied from 2300 to 12500:

$$\begin{aligned} &ZnO(c) + \tfrac{1}{3}[(n+2)H_3PO_4 + mH_2O](sln) \\ &\quad = \tfrac{1}{3}[3Zn^{2+} + 2PO_4^{3-} + 3H_2O](nH_3PO_4 + mH_2O)(sln) \qquad (1) \end{aligned}$$

The results are collected in Table 2 and a statistical test showed that there was no significant correlation between the enthalpy of reaction and the final concentration; hence the enthalpy of dilution of the products may be assumed to be less than the uncertainty interval of the experimental results.

Corresponding experiments with zinc phosphate anhydrate, dihydrate and tetrahydrate were performed giving approximately the same final concentrations in the excess H_3PO_4(aq); the reactions are described in eqns. (2)–(4) and the results are collected in Tables 3–5:

$$\begin{aligned} &Zn_3(PO_4)_2(c) + [nH_3PO_4 + mH_2O](sln) \\ &\quad = [3Zn^{2+} + 2PO_4^{3-}](nH_3PO_4 + mH_2O)(sln) \qquad (2) \end{aligned}$$

TABLE 3

Enthalpies of solution of $Zn_3(PO_4)_2$ in excess aqueous H_3PO_4 at 298.15 K (eqn. (2))

Mass [a] $Zn_3(PO_4)_2$ (g)	Mole ratio (H_2O:Zn^{2+})	$-\Delta H$ (kJ mol^{-1})
0.08896	8029	170.89
0.12402	5759	170.92
0.14460	4940	170.68
0.15075	4738	170.81
0.15150	4714	170.81
0.26782	2667	170.77
	$\langle -\Delta H\rangle \pm 2$(sdm) = 170.81 ± 0.09 kJ mol^{-1}	

[a] Mass in vacuo, $\rho(Zn_3(PO_4)_2) = 3.62$ g cm^{-3}.

TABLE 4

Enthalpies of solution of $Zn_3(PO_4)_2 2H_2O$ in excess aqueous H_3PO_4 at 298.15 K (eqn. (3))

Mass [a] $Zn_3(PO_4)_2 2H_2O$ (g)	Mole ratio (H_2O:Zn^{2+})	$-\Delta H$ (kJ mol^{-1})
0.09526	8198	141.46
0.11184	6983	141.58
0.12995	6010	141.55
0.22248	3510	141.48
0.23111	3379	141.55
0.25269	3091	141.77
	$\langle -\Delta H\rangle \pm 2$(sdm) = 141.58 ± 0.10 kJ mol^{-1}	

[a] Mass in vacuo, $\rho(Zn_3(PO_4)_2 2H_2O) = 3.29$ g cm^{-3}.

TABLE 5

Enthalpies of solution of $Zn_3(PO_4)_2 3.94H_2O$ (batch I) and $Zn_3(PO_4)_2 3.97H_2O$ (batch II) in excess aqueous H_3PO_4 at 298.15 K (eqn. (4))

Batch	Mass [a] (hydrate) (g)	Mole ratio (H_2O:Zn^{2+})	$-\Delta H$ [b] (kJ mol^{-1})
I	0.09565	8861	112.70
I	0.16275	5208	112.77
I	0.18760	4518	112.57
I	0.23423	3619	112.87
I	0.25889	3274	112.62
I	0.33395	2538	112.70
II	0.10627	7976	112.32
II	0.22565	3756	112.41
II	0.22971	3690	112.33
II	0.25227	3360	112.46
II	0.27523	3080	112.19
II	0.30317	2796	112.49

[a] Mass in vacuo, ρ(tetrahydrate) = 3.10 g cm^{-3} [1].

[b] Both batches have non-integral water:zinc phosphate stoichiometry and the ΔH results were corrected for this, assuming the presence of $Zn_3(PO_4)_2 2H_2O$ in each sample and using the ΔH in Table 4 to correct. $\langle -\Delta H$(batch I)$\rangle$ (kJ mol^{-1}) = 111.8 ± 0.1; $\langle -\Delta H$(batch II)$\rangle$ (kJ mol^{-1}) = 112.0 ± 0.1. A mean value was used in subsequent calculations.

TABLE 6

Standard enthalpies of formation of zinc orthophosphate and its hydrates at 298.15 K

Compound	$-\Delta H_f^\ominus$ (kJ mol^{-1}) (this work)	$-\Delta H_f^\ominus$ (kJ mol^{-1}) (literature)
$Zn_3(PO_4)_2(c)$	2891.2±3.3	2892.4 [23] 2898±10 [24] [a]
$Zn_3(PO_4)_2 2H_2O(c)$	3492.1±3.3	
$Zn_3(PO_4)_2 4H_2O(c)$	4093.5±3.3	4091.5±2.1 [25]

[a] Recalculated from ref. 24 using $\Delta H_f^\ominus$ [ZnO, c] = −350.46±0.27 kJ mol^{-1} [21].

$$Zn_3(PO_4)_2 2H_2O(c) + [nH_3PO_4 + mH_2O](sln) = [3Zn^{2+} + 2PO_4^{3-} + 2H_2O](nH_3PO_4 + mH_2O)(sln) \quad (3)$$

$$Zn_3(PO_4)_2 4H_2O(c) + [nH_3PO_4 + mH_2O](sln) = [3Zn^{2+} + 2PO_4^{3-} + 4H_2O](nH_3PO_4 + mH_2O)(sln) \quad (4)$$

The standard enthalpies of formation of the title compounds were derived using the following ancillary thermodynamic data: heats of formation, ZnO(c) (−350.46 ± 0.27) [21]; $H_2O(l)$ (−285.83 ± 0.04) [21]; $H_3PO_4 40H_2O(sln)$ (−1294.3 ± 1.6) [22]; $\Delta H(H_3PO_4 40H_2O \rightarrow H_3PO_4 69.8H_2O) = -0.38$ kJ mol^{-1} [23]. The derived results are compared with the available literature data in Table 6. The agreement between our result and that of Wagman et al. [23] is illusory; the origin of Wagman's value (tabulated 1967) is almost certainly the work of Meadowcroft and Richardson [24] which, when recalculated using the recent $\Delta H_f^\ominus$[ZnO, c] value (see above), differs from our result. Volkov [25] employed a similar "same final thermodynamic state" procedure to that described here except that the oxide was dissolved in a mixture of HCl and H_3PO_4 and the phosphate was dissolved in HCl. The agreement between our result and that of Volkov is satisfactory.

Batch microcalorimetry

In these experiments, the thermal response resulting from the hydration of either zinc orthophosphate or its dihydrate was measured; eqns. (5) and (6) represent the reactions studied

$$Zn_3(PO_4)_2(c) + (n+4)H_2O(l) = Zn_3(PO_4)_2 4H_2O(c) + nH_2O(l) \quad (5)$$

$$Zn_3(PO_4)_2 2H_2O(c) + (n+2)H_2O(l) = Zn_3(PO_4)_2 4H_2O(c) + nH_2O(l) \quad (6)$$

The product in each case was tetrahydrate and its identity was established by TGA of the residue after calorimetry; the thermal response was nearly identical to that given by the stock tetrahydrate prepared by Bishop's procedure (see the Experimental section above). The aqueous solubility of the tetrahydrate is so low [19] that the excess water ($n\text{H}_2\text{O}$ in eqns. (5) and (6)) is of no consequence. The rate at which reactions (5) and (6) proceed was quite different. For the dihydrate experiments (eqn. (6)) the thermal response following mixing into water was immediate and the reaction was complete after approximately 80 min; it was clear that the rate of heat output from the reaction was greater than the characteristic thermal response of the batch cell. For the hydration of the anhydrate, there was an irreproducible induction period (from 3 to 140 min) before hydration began. The time taken to reach maximum power output was an order of magnitude greater than for the dihydrate hydration experiments and the total time to completion of reaction was five times greater. One advantage of the induction period noted above is that the "blank effect" (see the Experimental section above) which is always immediate on initiation of mixing, was readily resolved from the hydration effect. Several experiments were completed in which the water was doped (at about 1% level) with a commercial dispersant (Dispex A40, Allied Colloids) to promote wetting of the zinc phosphate surface; this had no effect on the induction time and we conclude that the surface is adequately wetted. However, if the anhydrous material was doped with around 1% of solid tetrahydrate prior to reaction initiation, then the induction period was absent and the rate of hydration increased very sharply so as to resemble that for the dihydrate reaction. The results are collected in Table 7.

Using the enthalpies of formation of the anhydrous material and of the dihydrate from Table 6 in combination with the enthalpies of hydration in Table 7, two independent values for $\Delta H_f^{\ominus}[\text{Zn}_3(\text{PO}_4)_2 4\text{H}_2\text{O, c}]$ may be evaluated

$\Delta H_f^{\ominus}[\text{Zn}_3(\text{PO}_4)_2 4\text{H}_2\text{O, c}]$ (from eqn. (6)) $= -4088.3 \pm 3.4$ kJ mol^{-1};
$\Delta H_f^{\ominus}[\text{Zn}_3(\text{PO}_4)_2 4\text{H}_2\text{O, c}]$ (from eqn. (5)) $= -4086.6 \pm 3.8$ kJ mol^{-1}.

These two results are not significantly different from one another but are significantly different from the enthalpy of formation of the tetrahydrate in Table 6. It appears that the tetrahydrate produced by room temperature hydration of the dihydrate or of the anhydrous material is a polymorphic form distinct (thermodynamically) from that produced by a conventional synthetic procedure. The difference in the enthalpies of formation of the high energy polymorph and the normal form is 5.2 ± 1.0 or 6.8 ± 1.9 kJ mol^{-1} from two independent Hess' law cycles (see Fig. 1).

There is an extensive literature on polymorphic forms of $\text{Zn}_3(\text{PO}_4)_2$ $4\text{H}_2\text{O}$. In early work, Spencer [26] distinguished three forms (α-, β- and *para*-hopeite; hopeite is the naturally occurring mineral) on the basis of their refractive indices and their behaviour on thermal dehydration. The α form loses water in two distinct steps, at ≈ 110°C and ≈ 230°C, whereas the β form behaves like the α form at 110°C but then loses the remainder of its water continuously to 290°C. *para*-Hopeite loses water in a single

TABLE 7

Reaction times and enthalpy changes for the hydration at 298.15 K of zinc phosphate (eqn. (5)) and zinc phosphate dihydrate (eqn. (6))

Equation	Sample mass (mg)	t [a] (min)	τ [b] (min)	$-\Delta H$ (kJ mol^{-1})
6	11.2	14.6	82	24.9
6	20.7	12.0	70	23.4
6	20.8	14.2	80	23.3
6	21.1	13.4	83	26.7
6	21.5	13.0	68	24.9
6	29.3	10.8	94	24.1
		$\langle -\Delta H_6 \rangle \pm 2(\text{s.d.m}) = 24.5 \pm 1.0$ kJ mol^{-1}		
5	7.1	158	260	50.7
5	12.1	117	256	53.8
5	14.4	150	302	52.3
5 [c]	19.6	80	308	57.0 [d]
5 [c]	29.8	203	452	49.2
5 [c]	35.4	66	400	50.7
5	43.6	114	328	54.2
5	50.5	83	268	54.7
5 [c]	56.7	91	540	50.9
5	124.3	220	1200	52.8
		$\langle -\Delta H_5 \rangle \pm 2(\text{s.d.m}) = 52.1 \pm 1.9$ kJ mol^{-1}		

[a] t is the time from reaction initiation to maximum power output.

[b] τ is the time for complete reaction.

[c] These results were used to extract kinetic information (see the Results and Discussion section).

[d] This result was considered an outlier and not included in the mean.

step between 160 and 230°C. Subsequently, Hill and Milnes [27] reported that *para*-hopeite contains significant quantities of Fe, Mn and Mg and, hence, could not be considered as a zinc phosphate tetrahydrate polymorph. The X-ray diffraction literature on these materials is confused [4]; both α- and β-hopeite are orthorhombic. Hill and Jones [4] reviewed this literature and concluded "the X-ray powder diffraction spectra of all samples used (referring to a range of natural and synthetic hopeites) are indistinguishable and hence the non-hydrogen atom positions within the crystal are essentially identical and therefore the marked difference in thermal response primarily involves changes in hydrogen atom bonding alone". Among the synthetic hopeites made by Hill and Jones [4], a form with thermal characteristics similar to β-hopeite was prepared by digesting the zinc phosphate suspension at low pH (≤ 2). Finally, Higashi et al. [28] consider these materials as possible dental cements and distinguish two forms of tetrahydrate; form A which is water-settable on rehydration following dehydration, and form B which is not. Form A is prepared from ZnO and H_3PO_4 in a manner similar to that used in this work and the final

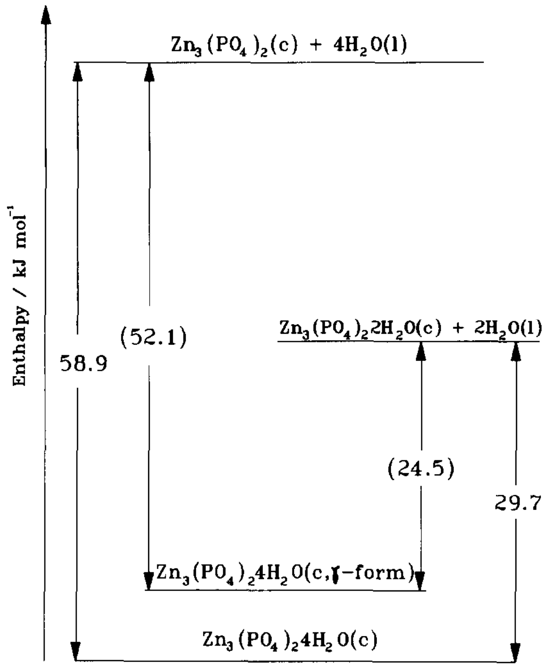

Fig. 1. Thermodynamic interrelation between zinc phosphate anhydrate, dihydrate and two forms of tetrahydrate. Results in parentheses are from batch microcalorimetry; others are differences from solution/reaction calorimetry. The difference in the heats of formation of the two tetrahydrate polymorphs is 6.8 ± 1.9 kJ mol^{-1} or 5.2 ± 1.0 kJ mol^{-1} from two independent Hess law cycles.

suspension is digested at 90°C, whereas form B is prepared similarly but digested at 15°C. Further, form A (water-settable, 90°C digestion) shows thermal dehydration characteristics similar to α-hopeite and form B (15°C digestion) resembles β-hopeite in this respect. We may assert with confidence that the tetrahydrate synthesised from ZnO and H_3PO_4(aq) in this work is α-hopeite but that the material made from the room temperature hydration of the anhydrate or of the dihydrate is not β-hopeite; it is a different polymorph characterised by its synthesis and different thermodynamic properties (we tentatively designate this form as γ-hopeite). The thermodynamic interrelation between $Zn_3(PO_4)_2$ and its hydrates is illustrated in Fig. 1.

As mentioned above the anhydrate hydration was slow compared to the dihydrate hydration and some of the batch microcalorimetry traces for eqn. (5) were processed to extract kinetic information. The extent of reaction at any time t ($\alpha(t)$) was set equal to the area beneath the thermal emf versus time curve at time t divided by the total area, i.e.

$$\alpha(t) = A_t/A_\infty \tag{7}$$

The $\alpha(t)$ curves thus generated were sigmoid in shape suggesting that an Avrami–Erofe'ev rate expression [29] would describe the results. The results for four runs (identified in Table 7) were fitted to standard rate expressions [30] and the best fit ($\langle s_b \rangle = 1.8\%$ [30]) was obtained for eqn. (8)

$$[-\ln(1-\alpha)]^{0.5} = k(t-t_0) \tag{8}$$

where $k = 0.010 \pm 0.003$ min^{-1} and t_0 is the induction time varying from 3 to 140 minutes. This rate equation is designated A2 [31] and is characteristic of the growth of hydration nuclei proceeding in one or two dimensions [32].

Bogoyavlenskaya et al. [33] report some "differential microcalorimetry" studies on a tetrahydrate phase called hopeite (probably α-hopeite) that involve measuring the enthalpy changes that accompany the dissolution of different hydrates in H_3PO_4(aq). The result is presented as a "binding strength (kcal per mole H_2O)" and assuming this refers to eqn. (9)

$$0.25Zn_3(PO_4)_2(c) + H_2O(l) = 0.25Zn_3(PO_4)_2 4H_2O(c) \tag{9}$$

then $\Delta H_9 = 0.25\Delta H_5$. Bogoyavlenskaya et al. [33] give ΔH_9 as -23.5 kJ mol^{-1} whereas from Table 7, $0.25\Delta H_5$ is -13.0 ± 0.5 kJ mol^{-1}; we can offer no explanation for this disagreement.

ACKNOWLEDGEMENTS

This work was supported by the MOD(PE) and the British Council. The authors gratefully acknowledge assistance with XRD powder diffraction patterns from Mr. George Seyd (ARE, Holton Heath) and helpful discussion from British Rail Technical Centre, Derby and Dr. A. Head.

REFERENCES

1 M. Farnsworth and C.H. Kline, Zinc Chemicals, Zinc Development Association, London, 1973.
2 F.L. Katnack and F.A. Hummel, J. Electrochem. Soc., 105 (1958) 125.
3 M.V. Goloshchapov and T.N. Filatova, Russ. J. Inorg. Chem., 14 (1969) 424.
4 R.J. Hill and J.B. Jones, Am. Mineral., 61 (1976) 987.
5 A.R. Milnes and R.J. Hill, Neues Jahrb. Mineral. Monatsh., 1 (1977) 25.
6 C. Calvo, Can. J. Chem., 43 (1965) 436.
7 S.A. Amirova, V.V. Pechkovskii and G.E. Tyuleneva, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol., 10 (1967) 3.
8 J.S. Stephens and C. Calvo, Can. J. Chem., 45 (1967) 2303.
9 C. Calvo, J. Phys. Chem. Solids, 24 (1963) 141.
10 J. Komrska and V. Satava, Silikaty, 13 (1963) 135, Chem. Abs., 72 4755j.
11 J. Barraclough and J.B. Harrison, J. Oil Colour Chem. Assoc., 48 (1954) 341.
12 J.B. Harrison, Corrosion and Coatings, 3 (1976) 11.
13 A.G. Kotlova, N.I. Shchepochkina and B.M. Kobtsev, Inorg. Mater. (USSR), 11 (1976) 1247.

14 D. Bishop, British Rail Technical Centre, Derby, pers. comm., February 1985.
15 British Standards, BS5193, 1975 with amendment 3207, 1980.
16 Joint Committee on Powder Diffraction Standards, 1601, Park Lane, Swarthmore, Pennsylvania 19081, USA.
17 S.J. Peake, Ph.D. Thesis, Univ. of London, 1976.
18 E.J. Prosen and M.V. Kilday, J. Res. Nat. Bur. Stand. Sect. A, 77 (1973) 581.
19 J.O. Nriagu, Geochim. Cosmochim. Acta, 37 (1973) 2357.
20 D. Elks, P.J. Gardner and I.W. McAra, unpublished work, 1985.
21 J.D. Cox, D.D. Wagman and V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Pub. Corp., London, 1989.
22 A.J. Head and G.B. Lewis, J. Chem. Thermodyn., 2 (1970) 701.
23 D.D. Wagman, W.H. Evans, V.B. Parker, R.A. Schumm, I. Halow, S.M. Bailey, K. Churney and R.N. Nuttall, J. Phys. Chem. Ref. Data Suppl., 11(2) (1982).
24 T.R. Meadowcroft and F.D. Richardson, Trans. Faraday Soc., 59 (1963) 1564.
25 A.I. Volkov, Khim. Khim. Tekhnol. (Minsk), 14 (1979) 58.
26 L.J. Spencer, Mineral. Mag., 15 (1908) 1.
27 R.J. Hill and A.R. Milnes, Mineral. Mag., 39 (1974) 684.
28 S. Higashi, K. Morimoto, A. Satomura, K. Horie, M. Anzai, K. Kimura, K. Takeda and T. Miyazima, J. Nipp. Univ. Sch. of Dentistry, 11 (1969) 60.
29 C.H. Bamford and C.F.H. Tipper (Eds.), Chemical Kinetics: Reactions in the Solid State, Vol. 22, Elsevier, London, 1980.
30 M.E. Brown and A.K. Galway, Thermochim. Acta, 29 (1979) 129.
31 J.H. Sharp, G.W. Brindley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.
32 Ref. 29, p. 57.
33 G.A. Bogoyavlenskaya, O.S. Krylov, G.N. Kas'yanova and N.A. Kalmykova, J. Appl. Chem. (USSR), 55 (1982) 1598.