Thermochimica Acta, 196 (1992) 117–123
Elsevier Science Publishers B.V., Amsterdam

The standard enthalpies of formation of some zinc orthophosphate polymorphs

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(Received 7 June 1991)

Abstract

The standard enthalpies of formation of polymorphic forms of $Zn_3(PO_4)_2$, $Zn_3(PO_4)_2$-$2H_2O$ and $Zn_3(PO_4)_24H_2O$ have been determined at 298.15 K. Their thermodynamic interrelation with the stable forms is discussed.

INTRODUCTION

The standard enthalpies of formation of $Zn_3(PO_4)_2$(cr), $Zn_3(PO_4)_2$ $2H_2O$(cr) and $Zn_3(PO_4)_24H_2O$(cr) have been reported recently from this laboratory [1]. During the course of this work it became clear that there are numerous polymorphs of these materials and an estimate of the heat of formation of a tetrahydrate polymorph (named the γ form) was included in the study. Two experimental techniques were used: reaction/solution calorimetry (RSC) and batch microcalorimetry (BMC), both at 298.15 K. In RSC, the enthalpy change of the reaction between ZnO and H_3PO_4(aq) was compared with the corresponding enthalpy change for the solution of a zinc phosphate in H_3PO_4(aq) to yield the same final thermodynamic state. By this procedure, detailed characterisation of the final thermodynamic state was unnecessary. In BMC, the enthalpy change accompanying the hydration of the anhydrate (or a dihydrate) to the tetrahydrate was measured directly.

The same experimental methods have been used for the studies reported here. The standard enthalpy of formation of $Zn_3(PO_4)_24H_2O$(cr, γ) is established unambiguously and, in addition, polymorphs of the anhydrate and dihydrate are characterised thermodynamically.

EXPERIMENTAL

Apparatus

The calorimeter and their testing have been described previously [1].

Materials

$Zn_3(PO_4)_2 2H_2O$(cr, active form) was prepared from a sample of the thermodynamically stable tetrahydrate (identified in ref. 1 as $Zn_3(PO_4)_2$-$3.94H_2O$ by gravimetric dehydration [2]) which was dehydrated by evacuation to 0.05 mmHg at 20 °C for 16 h; analysis by gravimetric dehydration showed it to be $Zn_3(PO_4)_2 2.00H_2O$ (the accuracy of this method of analysis is ± 0.02 in the molar ratio of H_2O to phosphate). It has been shown [3] that prolonged evacuation under the conditions described above causes no further dehydration.

$Zn_3(PO_4)_2$(cr, active form) was prepared by heating a sample of tetrahydrate in air to 550 °C for 65 h.

RESULTS AND DISCUSSION

The two experimental techniques used, reaction/solution calorimetry (RSC) and batch microcalorimetry (BMC), are complementary. Two reactions, studied by RSC and giving the same final thermodynamic state, are used to determine directly the heat of formation of a given hydrate. Experiments with BMC give the difference between the heats of formation of a lower hydrate and the tetrahydrate. Consequently, if the heat of formation of one hydrate is known from RSC then the heat of formation of the other may be inferred from the results of a BMC experiment.

$Zn_3(PO_4)_2 4H_2O(cr, \gamma$ form)

The procedure outlined above was used in previous work [1] to infer the heat of formation of the tetrahydrate γ form as -4086.6 ± 3.8 or -4088.3 ± 3.4 kJ mol^{-1}; these two estimates arise from separate BMC experiments starting with the thermodynamically stable anhydrate and dihydrate respectively. On immersion in water at room temperature these two materials each give the γ tetrahydrate which is thermodynamically less stable than the normal form by 6.8 ± 1.9 or 5.2 ± 1.0 kJ mol^{-1} respectively.

The γ form was prepared in situ in a calorimeter ampoule by mixing water (≈ 600 mg) with a known quantity (≈ 200 mg) of the thermodynamically stable dihydrate at ambient temperature. The mixture was left for 5 days, with occasional agitation, to ensure complete conversion to the tetrahydrate. These are the conditions, albeit with smaller samples (≈ 20 mg), which were used in the BMC experiments to produce the γ tetrahydrate reported earlier [1]. The reaction studied by RSC is given by the equation

$$[Zn_3(PO_4)_2 4H_2O(cr, \gamma) + xH_2O] + [nH_3PO_4 + mH_2O](sln)$$
$$= [3Zn^{2+} + 2PO_4^{3-} + 4H_2O](nH_3PO_4 + (m+x)H_2O)(sln) \qquad (1)$$

TABLE 1

Enthalpies of solution at 298.15 K of mixtures of zinc orthophosphate dihydrate and water in excess aqueous [a] H_3PO_4 (eqn. (1))

m(dihydrate) [b] (g)	$m_1(H_2O)$ (g)	$m_2(H_2O)$ (g)	$-Q_{exp}$ (J)	$-Q_{dil}$ (J)	$-Q_{corr}$ (J)	Mole ratio [d] H_2O: Zn^{2+}	$-\Delta H_1$ [c] (kJ mol^{-1})
0.11048	0.40780	0.39837	30.824	0.262	30.562	7068	116.76
0.12613	0.59200	0.58123	35.536	0.382	35.154	6191	117.64
0.16140	0.43923	0.42545	45.340	0.278	45.062	4838	117.84
0.17552	0.49279	0.47781	49.022	0.318	48.704	4449	117.12
0.24637	0.50730	0.48627	69.112	0.318	68.794	3170	117.86
0.29301	0.46944	0.44443	82.141	0.294	81.847	2665	117.90

[a] Initial concentration of H_3PO_4 was 0.795 M (or $H_3PO_4 69.8H_2O$) and was from the same batch as used in previous work [1].

[b] Mass in vacuo, ρ(dihydrate) = 3.29 g cm^{-3} [1].

[c] m_1 is the mass of water added and m_2 is the mass of excess H_2O; $m_2 = m_1 - 0.085363m$.

[d] Molar ratio of H_2O to Zn^{2+} in the final thermodynamic state.

[e] $\langle -\Delta H_1 \rangle \pm 2$(s.d.m.) = 117.5 ± 0.5 kJ mol^{-1}, uncertainty interval is ±2 (standard deviation from the mean).

The solubility of the tetrahydrate is vanishingly small [4] at near-neutral pH and ambient temperature so the first term of the initial thermodynamic state in eqn. (1) may be written as the immiscible mixture; as in the earlier study [1], the final thermodynamic state is nominally identified as containing Zn^{2+} and PO_4^{3-} only. The results of six experiments are collected in Table 1; Q_{exp} is the experimental enthalpy change, Q_{dil} is a correction term for the exothermic dilution of the excess H_2O (xH_2O in eqn. (1)) and $Q_{corr} = Q_{exp} - Q_{dil}$. Combination of ΔH_1 with the corresponding enthalpy change for the $ZnO + H_3PO_4$ reaction [1] to yield the same final thermodynamic state gives $\Delta H_f^{\ominus}[Zn_3(PO_4)_2 4H_2O(cr, \gamma)] = -4087.9 \pm 3.4$ kJ mol^{-1}; where the ancillary data for this calculation are given in ref. 1. This compares favourably with the two indirect estimates of this quantity given above; a weighted mean is $\Delta H_f^{\ominus}[Zn_3(PO_4)_2 4H_2O(cr, \gamma)] = -4087.8 \pm 3.4$ kJ mol^{-1} and the difference in the heats of formation of the γ form and the thermodynamically stable tetrahydrate is 5.7 ± 0.5 kJ mol^{-1}.

$Zn_3(PO_4)_2 2H_2O$(cr, β form)

Kotlova et al. [5] have prepared a dihydrate polymorph and have characterised it by thermal analysis and powder XRD. They designate this polymorph as "active" form in that it is more hygroscopic than the normal dihydrate (called the α form) to which it converts at ≈ 150 °C at ambient pressure; the synthetic route is via dehydration of the tetrahydrate at the lowest possible temperature. Our sample of "active" dihydrate (designated

TABLE 2

Enthalpy changes for the solution of $Zn_3(PO_4)_22H_2O(cr, \beta)$ in excess aqueous H_3PO_4 (eqn. (2)) and for its hydration in excess liquid water (eqn. (3)) at 298.15 K

Equation	$m(Zn_3(PO_4)_2$-$2H_2O\ (\beta)$ [a] (g)	Mole ratio $H_2O:Zn^{2+}$	$-\Delta H_2$ [b] (kJ mol^{-1})	$-\Delta H_3$ [c] (kJ mol^{-1})
(2)	0.28504	2740	146.2	
(2)	0.20867	3743	146.2	
(2)	0.11485	6800	146.3	
(3) [d]	0.0331	–		29.5
(3) [d]	0.0264	–		28.4

[a] Mass in vacuo, $\rho \approx 3.3$ g cm^{-3} [1].

[b] $\langle -\Delta H_2 \rangle = 146.2$ kJ mol^{-1} (estimated error ± 0.5 kJ mol^{-1}).

[c] $\langle -\Delta H_3 \rangle = 29.0$ kJ mol^{-1} (estimated error ± 0.5 kJ mol^{-1}).

[d] For these BMC experiments, the time to maximum power output was around 1 min and the total hydration time was around 1500 min.

β form) was prepared by dehydration of the tetrahydrate at reduced pressure and ambient temperature (see Experimental section) and it is likely that our β form is the same as Kotlova et al.'s active form. The results of an RSC study (eqn. (2), below) and two BMC experiments (eqn. (3)) for the β form are collected in Table 2.

$$[Zn_3(PO_4)_22H_2O(cr, \beta)] + [nH_3PO_4 + mH_2O](sln)$$
$$= [3Zn^{2+} + 2PO_4^{3-} + 2H_2O](nH_3PO_4 + mH_2O)(sln) \qquad (2)$$

$$Zn_3(PO_4)_22H_2O(cr, \beta) + (p+2)H_2O(l)$$
$$= Zn_3(PO_4)_24H_2O(cr) + pH_2O(l) \qquad (3)$$

Combining ΔH_2 from Table 2 with the corresponding enthalpy change for the $ZnO + H_3PO_4$ reaction [1] gives $\Delta H_f^{\ominus}[Zn_3(PO_4)_22H_2O(cr, \beta)] = -3487.6 \pm 3.4$ kJ mol^{-1}. The corresponding value for the normal (or α) form is -3492.1 ± 3.3 kJ mol^{-1} and consequently $\Delta H(\alpha \rightarrow \beta) = 4.5 \pm 0.2$ kJ mol^{-1}; the uncertainty interval for the difference is much smaller than for either component as the error (± 3.3 kJ mol^{-1}) in the heat of formation of the final thermodynamic state of eqn. (2) cancels in the evaluation of the difference.

Combining the heat of formation of the dihydrate (β form) with the heat change for reaction (3) in Table 2 gives $\Delta H_f^{\ominus}[Zn_3(PO_4)_24H_2O, cr] = -4088.3 \pm 3.4$ kJ mol^{-1}. This is not significantly different from the weighted mean for $\Delta H_f^{\ominus}[Zn_3(PO_4)_24H_2O, cr, \gamma]$ reported above and hence this experiment identifies the tetrahydrate produced in the BMC experiments with the dihydrate β form as the γ form. These γ tetrahydrate samples were separated at the end of the BMC experiments and examined by thermogravimetry; a two-stage mass loss, 2 moles at 88 ± 16 °C and a

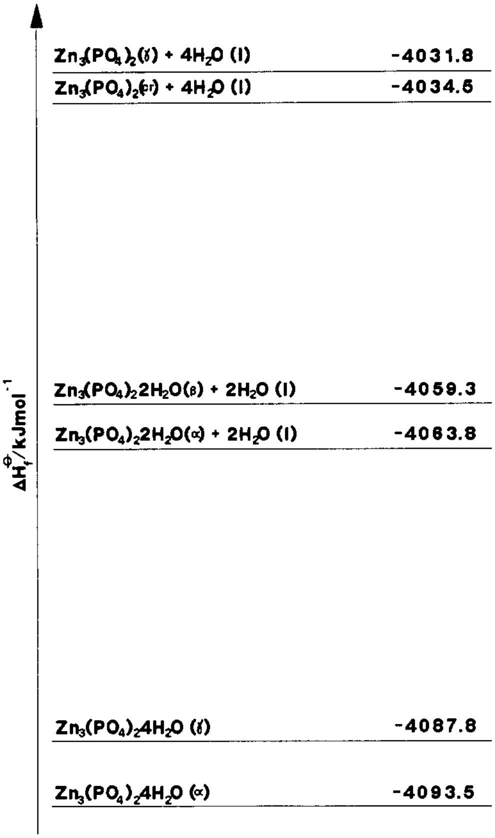

Fig. 1. Molar enthalpies of formation of zinc orthophosphate and its hydrates (approximately to scale).

further two moles at 296 ± 11 °C was noted. This is characteristic of the normal tetrahydrate [1,6] and consequently the γ form of the tetrahydrate is distinguished by its thermodynamics rather than by its behaviour on thermal dehydration [1], a kinetic property.

$Zn_3(PO_4)_2$*(cr, γ form)*

The conventional procedure for the synthesis of the anhydrate is dehydration of any orthophosphate hydrate at 550 °C for 5 h according to BS 5193 [2]. Kotlova et al. [5] have noted that the rehydration characteristics of anhydrates produced at successively higher dehydration temperatures vary considerably; they distinguish between a "transitional hygroscopic phase" obtained by dehydration between 350 and 600 °C and a "stable α form" obtained at higher temperatures ($\leq$ 900 °C). At 942 °C, there is a well established [7,8] reversible polymorphic transition to a β form. Also, Higashi et al. [9] distinguished two forms of anhydrate, one water-settable

TABLE 3

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

Formula	$-\Delta H_f^\ominus$ (kJ mol^{-1})	Ref.
$Zn_3(PO_4)_2$(cr, γ)	2888.5 ± 3.4	This work
$Zn_3(PO_4)_2$(cr)	2891.2 ± 3.3	1
$Zn_3(PO_4)_2 2H_2O$(cr, β)	3487.6 ± 3.4	This work
$Zn_3(PO_4)_2 2H_2O$(cr, α)	3492.1 ± 3.3	1
$Zn_3(PO_4)_2 4H_2O$(cr, γ)	4087.8 ± 3.4	1, this work
$Zn_3(PO_4)_2 4H_2O$(cr, α)	4093.5 ± 3.3	1

on rehydration and another form not water-settable. We have explored the thermodynamic effect of prolonged dehydration of the tetrahydrate at 550 °C (see Experimental section). The material thus produced (we designate this the γ form) was examined by RSC according to

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

Only two experiments were performed with sample masses of around 130 mg, yielding a solution with final $H_2O:Zn^{2+}$ molar ratio of approximately 5500 and $\Delta H_4 = -173.6 \pm 0.5$ kJ mol^{-1}; the uncertainty interval was estimated. Combining this result with the corresponding ΔH for $ZnO + H_3PO_4$ experiments [1] gives $\Delta H_f^\ominus[Zn_3(PO_4)_2(cr, \gamma)] = -2888.5 \pm 3.4$ kJ mol^{-1}; this is 2.7 ± 0.2 kJ mol^{-1} less exothermic than the $\Delta H_f^\ominus$ for the normal form produced by BS 5193 [2]. A γ form of the anhydrate has been recorded previously [10] but it contained significant quantities of Mn^{2+} so cannot be regarded as a true zinc orthophosphate.

The thermodynamic interrelationships between the new polymorphs described here and the previously characterised forms [1] are shown in Fig. 1 and the heats of formation are collected in Table 3.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from the MOD (PE) and the British Council.

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