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Thermochemistry of the mixed calcium phosphate $Ca_8P_2O_7(PO_4)_4$

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ABSTRACT

The calcium mixed phosphate $Ca_8P_2O_7(PO_4)_4$ has been synthesized by thermal decomposition of octacalcium phosphate previously prepared by precipitation in ammoniacal phosphate solution. The enthalpy of formation at 298.15 K referenced to β-tricalcium phosphate and calcium pyrophosphate is determined. β-Tricalcium phosphate was prepared by two methods: precipitation in ammoniacal aqueous medium and high temperature solid-state reaction. Calcium pyrophosphate was prepared by high temperature solid-state reaction. All the compounds are characterized by chemical analysis, X-rays diffraction and IR spectroscopy. The enthalpy of formation $+10.83 \pm 0.63\ \text{kJ mol}^{-1}$ is obtained by solution calorimetry at 298.15 K in nitric acid.

1. Introduction

Phosphates constitute a noteworthy family of chemical compounds generally characterized by a great thermodynamical stability. The structures of phosphate compounds allow various substitutions of cationic and anionic groups and thus, give rise to new families of phosphatic materials of great importance in chemical and natural sciences. In the natural aqueous milieu the major part of the phosphates precipitates in the hydroxyapatite form in which numerous ionic substitutions may occur [1]. Substituted apatites are very important compounds in geology and in life science [2,3]. The industrial and biological applications are numerous, e.g. in fertilizers, treatment of liquid waste, in toothpaste and ceramics, and for coating prosthesises [4–6].

PO_4^{3-} anions and hydrogenphosphate anions HPO_4^{2-} are both present in the structure of the octacalcium phosphate $Ca_8(HPO_4)_2(PO_4)_4{\cdot}5H_2O$ (OCP). OCP participates as precursor in the precipitation of hydroxyapatite in water [7–9] or non-aqueous phase [10]. Anhydrous OCP has been synthesized by Bonel and co-workers in a mixture of water–ethanol [11]. The thermal decomposition of the HPO_4^{2-} ions causes the condensation to $P_2O_7^{4-}$ groups and then leads to a calcium phosphate-diphosphate of chemical formula $Ca_8P_2O_7(PO_4)_4$ containing both PO_4^{3-} and $P_2O_7^{4-}$ anions [12]. This phase has also been synthesized in anhydrous ethanol by thermal decomposition of $Ca_8(HPO_4)_2(PO_4)_4{\cdot}x\text{EtOH}$ [13].

The structures and methods for the synthesis of many phosphatic compounds are already well known. But very few experimental thermochemical studies have been undertaken. In comparison with silicates, phase equilibria data and thermodynamic functions of phosphatic phases are scarce. Some estimates of the standard enthalpies of formation have been proposed by Latimer [14] or Le Van [15]. However most are based on additive properties and the estimates do not take into account higher order interactions. For phase diagram calculations such an uncertainty is not acceptable. This work determines experimentally the enthalpy of formation of $Ca_8P_2O_7(PO_4)_4$ at 298.15 K relative to tricalcium phosphate $Ca_3(PO_4)_2$ and pyrophosphate $Ca_2P_2O_7$.

2. Elaboration of the compound and the references

2.1. *β-Tricalcium phosphate*

The β-tricalcium phosphate (βTCP) has been synthesized by two different methods:

The double decomposition, or wet processing method, recommended by Heughebaert and Montel reacts calcium nitrate and ammonium monohydrogenphosphate dissolved in an ammoniacal solution at pH 10. A jelly-like precipitate was obtained and dried at 353 K and then calcined at 1173 K during 24 h [16].

By reacting calcium carbonate (>98.5% purity) with ammonium phosphate (>99% purity) in a 3:2 mole ratio. The finely crushed mixture is then gradually heated in platinum crucible to remove CO_2, NH_3 and H_2O, and then calcined at 773 K for a few hours and at 1173 K for 1 week with daily crushings in the presence of acetone.

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2.2. Calcium pyrophosphate

Calcium pyrophosphate was synthesized by solid-state reaction between calcium carbonate (>98.5% purity) and ammonium phosphate (>99% purity) in a 1:1 mole ratio. The same heat treatment as for tricalcium phosphate is applied to the finely crushed sample. The calcined product at 1173 K was well crystallized.

2.3. Calcium phosphate-diphosphate

The calcium phosphate-diphosphate $Ca_8P_2O_7(PO_4)_4$ was obtained by thermal decomposition at 953 K of the octacalcium phosphate $Ca_8(HPO_4)_2(PO_4)_4{\cdot}5H_2O$ [17] which was synthesized by a rapid precipitation at 310 K of a diammonium phosphate solution by a calcium nitrate solution in an equal volumes ethanol–water mixture. The diammonium phosphate solution consists of 30 mmol of diammonium phosphate dissolved in 250 ml of decarbonated water, added to 95 ml of ethanol and 45 ml of 28 wt% ammonia solution (density 0.92). The calcium nitrate solution contains 30 mmol of calcium nitrate dissolved in 100 ml of decarbonated water and 100 ml of ethanol [12]. The obtained precipitate is quickly filtered on a Büchner cap and then washed with a basic solution containing 180 ml of decarbonated water, 210 ml of ethanol and 30 ml of an ammonia solution. The product was then dried at 353 K during 24 h and the thermal decomposition of the precipitate carried out in a tubular oven under a 3 l/h flow of high purity helium at a 200 K/h heating rate up to 953 K. The final product is $Ca_8P_2O_7(PO_4)_4$.

Note that obtaining pure calcium phosphate-diphosphate without βTCP imposes an ionic $CO_3^{2-}/PO_4^{3-}+CO_3^{2-}$ ratio less than 0.077. The CO_3^{2-} ions react with the HPO_4^{2-} and the $P_2O_7^{4-}$ ions providing PO_4^{3-} ions according to following reactions [18]:

$$2HPO_4^{-2} \rightarrow P_2O_7^{-4} + H_2O$$

$$P_2O_7^{-4} + CO_3^{-2} \rightarrow 2PO_4^{-3} + CO_2$$

$$HPO_4^{-2} + CO_3^{-2} \rightarrow PO_4^{-3} + CO_2 + OH^-$$

$$P_2O_7^{-4} + 2OH^- \rightarrow 2PO_4^{-3} + H_2O$$

3. Characterization of the samples

3.1. Infrared spectroscopy

Infrared spectra were recorded between 4000 and 400 cm^{-1} by a PerkinElmer FTIR 1000. The transparent pellets were prepared according to Hannah and Swinehart: one milligram of sample were mixed with 300 mg of potassium bromide, homogenized and compacted under vacuum up to about 750 MPa [19].

The recorded spectra are reported in Fig. 1 in Supplementary Data. They did not show characteristic bands of chemical groups which may be present as impurities:

- for the tricalcium phosphate the HPO_4^{-2} bands (1180–1200 and 875 cm^{-1}), the CO_3^{2-} bands (1410–1450 and 860–885 cm^{-1}) and the $P_2O_7^{4-}$ bands (1200–1250 cm^{-1});
- for the pyrophosphate the HPO_4^{-2} and CO_3^{2-} bands;
- for the calcium phosphate-diphosphate the PO_4^{3-} ions in the tricalcium phosphate band at 940 cm^{-1}. For calibration, mixtures of 5 and 10 wt% tricalcium phosphate in $Ca_8P_2O_7(PO_4)_4$ have been tested. The 940 cm^{-1} band is present in the 10 wt% pattern but miss in the 5 wt% one.

The bands at 930, 875, 855, 705 and 687 cm^{-1} are characteristic of $Ca_8P_2O_7(PO_4)_4$ as shown in Fig. 1 in Supplementary Data [17].

3.2. X-ray diffraction

The powder X-ray patterns were obtained with a Philips PW 3710 diffractometer with a copper anticathode.

Diffractograms of the βTCP and the pyrophosphate prove the products are crystalline. The diffractogram of the βTCP sample is consistent with that of a structure crystallizing in the rhombohedral system, *R*-3*c* space group and the following unit cell parameters, a = 10.429(1) Å and c = 37.3875(6) Å [20]. The XRD pattern of the pyrophosphate is that of a tetragonal structure of $P4_1$ space group and with the crystallographic parameters a = 6.684(6) Å and c = 24.145(15) Å [20]. The diffractograms are in good agreement with the βTCP and pyrophosphate ASTM files.

The powder diffraction pattern of the $Ca_8P_2O_7(PO_4)_4$ compound was recorded at a 0.02°(2θ) step and a 32 s/step counting times. The interreticular distances and the corresponding intensities are reported in Table 1 in Supplementary Data. The pattern was indexed by means of the TREOR [21], ITO [22] and DICVOL [23] computer programs. The structure is triclinic with the following crystallographic parameters: a = 12.987 Å; b = 14.481 Å; c = 6.775 Å; α = 101.32°, β = 90.21° and γ = 112.02°. Simulation of the structure by the FULLPROF program used in full pattern matching mode showed good agreement with the experimental diagram [24]. All the peaks are indexed, confirming the high purity of the product. Full structure determination will be the subject of a further study.

3.3. Chemical analysis

Calcium was determined by complexometry. An excess of EDTA was added to the acid solution containing the Ca^{2+} ions [25] and back-titrated with a standard solution of Zn^{2+} in an ammoniacal medium with Erichrome black T as indicator. The relative estimated error is about 0.5% (theoretical error 0.25%).

Phosphorus was analysed by colorimetry of PO_4^{3-} ions complexed with the vanadium molybdate, according to the Gee and Deitz method [26]. Measurements of the optical densities were carried out at 460 nm. The relative estimated error is about 0.5% (theoretical error 0.2%). The results in terms of Ca/P_{total} ratio are in good agreement with the expected theoretical values, respectively 1.504, 1.002, 1.333 (theoretical: 3/2, 1, 4/3). For $Ca_8P_2O_7(PO_4)_4$, pyrophosphate was hydrolyzed in $HClO_4$ 12 M at 373 K. The amount was determined by difference between PO_4^{3-} measured in the solution before and after the hydrolysis. The PO_4^{3-}/P_{total} and $P_2O_7^{4-}/P_{total}$ ratios found are, respectively 0.667 and 0.165 (theoretical 2/3, 1/6).

4. Thermochemical study

The enthalpy of formation is determined by isothermal solution calorimetry by dissolving in a suitable solvent (S) at the same temperature 298.15 K, separately, $Ca_8P_2O_7(PO_4)_4$ and a stoichiometric mixture of the reference compounds $2Ca_3(PO_4)_2 + Ca_2P_2O_7$. The enthalpy of formation in the standard conditions $\Delta_f H$ of $Ca_8P_2O_7(PO_4)_4$ is then determined according to the reaction:

$$2Ca_3(PO_4)_2(c) + Ca_2P_2O_7(c) \rightarrow Ca_8P_2O_7(PO_4)_4(c) \quad \Delta_f H \qquad (1)$$

where the enthalpies of the two dissolution reactions in acid are measured:

$$2Ca_3(PO_4)_2(c) + Ca_2P_2O_7(c) + 16H^+ \rightarrow 8Ca^{+2}(aq) + 4H_3PO_4(aq) + H_4P_2O_7(aq) \quad \Delta_{sol}H_2 \qquad (2)$$

$$Ca_8P_2O_7(PO_4)_4(c) + 16H^+ \rightarrow 8Ca^{+2}(aq) + 4H_3PO_4(aq) + H_4P_2O_7(aq) \quad \Delta_{sol}H_3 \tag{3}$$

The enthalpy of formation from the solution enthalpies with:

$$\Delta_f H = \Delta_{sol}H_2 - \Delta_{sol}H_3 \tag{4}$$

The products of the reaction of dissolutions (2) and (3) are identical if the concentrations of species are identical in reaction (2) and (3) and if final thermodynamic equilibrium is reached in the solution.

Dissolutions in various acids and combinations of acids at various concentrations (HCl, HNO_3, H_3PO_4, ...) have been tested. In nitric acid, the dissolution rate of calcium phosphates, in particular the pyrophosphates, depends on the concentration in aqueous solution. For concentrations of HNO_3 in the range 5–48 wt%, the kinetics of dissolution of the tricalcium phosphate do not vary but the rate of dissolution of the pyrophosphate decreases by a factor of five. The dissolutions were observed to be complete and fastest in 10 wt% nitric acid, which was chosen as solvent.

4.1. Calorimeter

The calorimetric measurements were carried out in the “Calset” calorimeter similar to the “Calsol” one described elsewhere [27]. The closed measurement cell, made of fluoride resin allows dissolutions in all mineral acidic or basic aqueous solutions. Its total capacity is 10 ml and commonly 8 ml of solvent are used. The stirring rate was 3 rpm.

The calorimeter is in a thermally regulated room at ±0.1 K. The thermal stability is better than ±1 mK and the dissolutions are carried out at 298.15 ± 0.01 K. Before dissolution, the solute and the solvent are whole isolated each together in two distinct compartments separated by a platinum cap and a *n*-decane liquid joint. The acidic vapor cannot react with the solute during the thermal stabilization time of the calorimeter. After thermal equilibrium, approximately 5 h, the solute is put in contact with the solvent by rotating the calorimeter. The dissolution starts with the first rotation.

The rotation of the calorimeter is stopped as soon as the flow of energy produced by the reaction is cancelled. The data acquisition is stopped about half an hour after the end of the dissolution so the final thermal and mechanical state of the calorimeter is identical to the initial state.

During dissolution the calorimetric signal proportional to the heat flux released by the reaction, is recorded and integrated by means of software control. The calibration factor of the calorimeter was 16.30 μW/μV, determined from several series of dissolutions carried out in the same range of amplitude of the signal and for the same duration of experiments with THAM dissolution or dilution in HCl [27]. The difference between the initial and final base lines is at most 0.5 μV. Before the integration a base line correction is added if necessary.

4.2. Solution enthalpies $\Delta_{sol}H^T$

The molar solution enthalpy is obtained by simple proportionality according to $\Delta_{sol}H = \sigma A/n$, where A is the integral of the thermogram in the whole interval of the reaction (in μV s), n is the number of mole of the dissolved sample, and σ is the calibration factor of the calorimeter.

The results of dissolution versus the concentration of the solutes $Ca_8P_2O_7(PO_4)_4$, the mechanical mixture $2Ca_3(PO_4)_2 + Ca_2P_2O_7$ and the separate references $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$ in the bath are reported in Tables 2–5 in Supplementary Data. The stoichiometries of the mixtures are realized at ±0.1% by weighing. The samples are weighed with a Mettler microbalance of 0.001 mg precision.

For each concentration, the random uncertainty is estimated assuming the normal distribution.

4.3. Enthalpy of formation $\Delta_f H^T$ of $Ca_8P_2O_7(PO_4)_4$

The method of constrained least squares is applied to data [28]. For each compound and mechanical mixture, the results reveal a linear dependence of the molar enthalpies of dissolution with the concentration within the 0.3–2.5 mmol/l range. Thus, a function $\Delta_{sol}(H_e)_i = ac_i + \Delta_{sol}(H_\infty)$ was fit to each series of data where $\Delta_{sol}(H_\infty)$ is the apparent solution enthalpy at infinite dilution.

The enthalpy of formation $\Delta_f H$ of $Ca_8\ P_2O_7(PO_4)_4$ is deduced from the terms $\Delta_{sol}(H_\infty)$.

$$\Delta_{sol}H(Ca_8P_2O_7(PO_4)_4) = (-286.19 + 0.454c) \pm 0.33\ \mathrm{kJ\,mol^{-1}}. \tag{5}$$

$$\Delta_{sol}H(Ca_2P_2O_7 + 2Ca_3(PO_4)_2) = (-275.36 + 0.454c) \pm 0.53\ \mathrm{kJ\,mol^{-1}} \tag{6}$$

The enthalpy of formation of $Ca_8P_2O_7(PO_4)_4$ is then deduced as +10.83 kJ mol^{-1} with a standard deviation ±0.63 kJ mol^{-1}.

Dissolutions of $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$ have been aside performed. The results are linearly fitted in the composition range as:

$$\Delta_{sol}H(Ca_3(PO_4)_2) = (-124.58 + 0.206c) \pm 0.76\ \mathrm{kJ\,mol^{-1}}. \tag{7}$$

$$\Delta_{sol}H(Ca_2P_2O_7) = (-34.683 + 0.682c) \pm 0.39\ \mathrm{kJ\,mol^{-1}} \tag{8}$$

The result of 2 × (7) + (8) = (−59.599–1.0934c) ± 0.26 kJ mol^{-1} differ from the enthalpy of dissolution of the mechanical mixture ($Ca_2P_2O_7 + 2Ca_3(PO_4)_2$) in Eq. (6). That means that the ionic equilibria in nitric solution resulting from the dissolution of the mechanical mixture and from the separate dissolutions of $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$ are different and then, the exact enthalpy of formation of $Ca_8P_2O_7(PO_4)_4$ must be calculated from the difference of Eqs. (5) and (6) and not from Eqs. (5), (7) and (8).

5. Discussion and conclusion

Considering the standard enthalpies of $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$, respectively −4120 and −3333 kJ mol^{-1} [29], the standard molar enthalpy of formation of $Ca_8P_2O_7(PO_4)_4$ is −11562 ± 1 kJ mol^{-1}.

For phosphate compounds, Le Van’s method of estimation of the standard enthalpy of formation based on an additivity law of cationic and anionic contributions has been proposed by Ait-Hou et al. [30]. The accuracy is generally within ±4%, but for $Ca_2P_2O_7$ is only ±2% and for $Ca_3(PO_4)_2$ is only ±0.3%, or respectively, 67 and 13 kJ mol^{-1}. In the model the $PO_4{}^{-3}$ and $P_2O_7{}^{-4}$ anions are independent and the anionic constants are $A(PO_4{}^{-3}) = -849$ kJ mol^{-1} and $A(P_2O_7{}^{-4}) = 1698$ kJ mol^{-1}, the cationic constant is $A(Ca^{+2}) = -858$ kJ mol^{-1}. The calculated standard enthalpy of formation of $Ca_8P_2O_7(PO_4)_4$, −11958 kJ mol^{-1} differ of ±1.7% from the experimental value. This good agreement is mainly due to the good agreement for the estimations of $Ca_2P_2O_7$ and $Ca_3(PO_4)_2$ and the low enthalpy of formation of $Ca_8P_2O_7(PO_4)_4$ relatively to these compounds.

The entropy at 298.15 K can be estimated following the Latimer’s model by additivity of the standard entropies of the references

$Ca_2P_2O_7$ and $Ca_3(PO_4)_2$: 661.22 J mol^{-1} K^{-1} [14,29], as for standard enthalpy, no interaction between the anions is introduced. The Gibbs energy is calculated at −11760 kJ mol^{-1} for formation of $Ca_8P_2O_7(PO_4)_4$ from the elements.

From the phase equilibria point of view it is important to estimate the degree of stability of $Ca_8P_2O_7(PO_4)_4$ versus the references $Ca_2P_2O_7$ and $Ca_3(PO_4)_2$. The enthalpy of formation has been found slightly positive and in the following enthalpy and entropy will be assumed to remain constant with temperature. The mixed compound has been elaborated at 953 K, that imposes a standard entropy of at least 11.4 J mol^{-1} K^{-1} for stabilization. Configurational mixing entropy may be a possible source of stabilization.

The fine structure of $Ca_8P_2O_7(PO_4)_4$ has not been already resolved and some assumption must be formulated. As the enthalpy of formation versus the βTCP and the calcium pyrophosphate references is very low, it can be assumed that the cationic environments of $(PO_4)^{-3}$ and $(P_2O_7)^{-4}$ anions found in respectively the βTCP and the calcium pyrophosphate are not deeply altered and are kept as two cationic distinguishable sublattices in $Ca_8P_2O_7(PO_4)_4$. A random distribution of the Ca cations on these sublattices leads to a mixing entropy of 37.5 J mol^{-1} K^{-1} which be sufficient to account for the stability of the phase. Further investigations are necessary to ensure an accurate knowledge of the fine structure.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.04.021.

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