Enthalpies of Formation of Compounds in the P_2O_5−CaO−H_2O System

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The enthalpies of formation were determined for $Ca_4(PO_4)_2O$, α-$Ca_3(PO_4)_2$, and the hydroxyapatite compositions $Ca_{10}(PO_4)_6(OH)_2$ and $Ca_9(HPO_4)(PO_4)_5OH$ by the analysis of isothermal calorimetric results obtained at 37.4 °C. Both hydroxyapatite compositions were formed by reaction of $Ca_4(PO_4)_2O$ with $CaHPO_4$ or with $CaHPO_4\cdot2H_2O$ in water depending on the molar proportions of the reactant used. $Ca_9(HPO_4)(PO_4)_5OH$ was also formed by direct hydrolysis of α-$Ca_3(PO_4)_2$ in water. Enthalpy of formation values were calculated by a Hess's Law analysis using several sets of equations. In summary, the enthalpy of formation values are: for $Ca_4(PO_4)_2O$, $-476_{2.4}$ kJ/mol, for α-$Ca_3(PO_4)_2$, $-409_{6.5}$ kJ/mol, for $Ca_9(HPO_4)(PO_4)_5OH$, $-127_{19.7}$ kJ/mol, and for $Ca_{10}(PO_4)_6(OH)_2$, $-137_{44.0}$ kJ/mol at 37.4 °C.

1. Introduction

Hard human tissues, teeth and bone, are composite materials primarily composed of impure, carbonated, calcium-deficient hydroxyapatite (HAp) and collagen. Stoichiometric hydroxyapatite is $Ca_{10}(PO_4)_6(OH)_2$.[1] However, hydroxyapatite exists over a range of compositions that may be characterized in terms of a Ca/P ratio with that of stoichiometric HAp being 1.67. Stable compositions may have Ca/P ratios extending to 1.5: $Ca_9(HPO_4)(PO_4)_5OH$. In general, HAp is $Ca_{(10-x)}(PO_4)_{(6-x)}(HPO_4)_x(OH)_{(2-x)}$, where x ranges from 0 to 1. Although it has also been reported that HAp, $Ca_{(10-x)}(PO_4)_{(6-x)}(HPO_4)_x(OH)_{(2-x)}$ (where x is 2), having a Ca/P ratio as low as 1.33,[2] may exist metastably, our work does not confirm this. Structurally, HAp contains two types of calcium sites.[3] Four of the calcium sites per unit cell are nine-coordinated. Six of the calcium sites per unit cell are seven-coordinated. Calcium deficiency results in the formation of up to one vacancy per unit cell on one of these seven-coordinated calcium sites.[4] Charge balance is maintained by the removal of one of the hydroxyl oxygens. The remaining proton becomes bound to an oxygen that is also coordinated with a phosphate.

Associated with its biocompatibility, there is continuing interest in hydroxyapatite-based prostheses[5] for applications involving orthopedics[6,78] and dentistry.[9,10] There is, in addition, interest in coating the surfaces of metallic prostheses with hydroxyapatite as a means to promote bone intergrowth, thereby improving the bond between native tissue and prosthesis.[11,12] However, each of the applications enumerated has traditionally employed HAp prepared by high-temperature processing and shaping prior to its use. In scheduled procedures, where the use of HAp can be anticipated, the processing requirement may not be a disadvantage. In procedures that must be performed as a result of trauma, such a restriction is an obvious disadvantage. Consequently, methods have been identified by which HAp monoliths can be formed at physiological temperature. These typically involve acid−base reaction between particulate calcium phosphate precursors or direct hydrolysis of a particulate solid calcium phosphate lacking a true solubility.

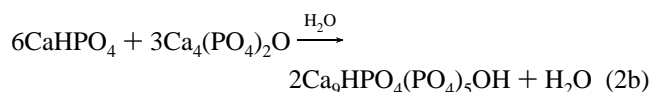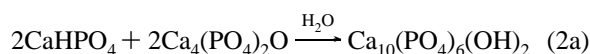The following illustrate reactions demonstrated to produce HAp at physiological temperature. The formation of stoichiometric HAp (SHAp) by an acid−base reaction between particulate dicalcium phosphate dihydrate ($CaHPO_4\cdot2H_2O$) and tetracalcium phosphate ($Ca_4(PO_4)_2O$) in water, as first described by Brown and Chow,[13] is illustrated is eq 1a:

$$2CaHPO_4\cdot2H_2O + 2Ca_4(PO_4)_2O \xrightarrow{H_2O}$$
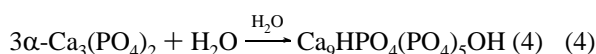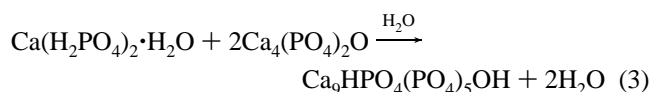$$Ca_{10}(PO_4)_6(OH)_2 + 4H_2O \quad (1a)$$
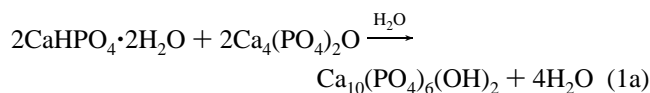
Equimolar proportions of the particulate acidic and basic calcium phosphates react to form stoichiometric HAp. Our work[14,15] has demonstrated that calcium-deficient HAp (CDHAp, Ca/P = 1.5) can also be produced:

$$6CaHPO_4\cdot2H_2O + 3Ca_4(PO_4)_2O \xrightarrow{H_2O}$$
$$2Ca_9HPO_4(PO_4)_5OH + 13H_2O \quad (1b)$$
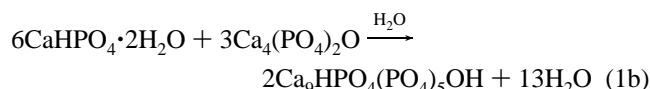
Reactions similar to those in eq 1, but involving anhydrous dicalcium phosphate (DCP), also produce HAp:

$$2CaHPO_4 + 2Ca_4(PO_4)_2O \xrightarrow{H_2O} Ca_{10}(PO_4)_6(OH)_2 \quad (2a)$$

$$6CaHPO_4 + 3Ca_4(PO_4)_2O \xrightarrow{H_2O}$$
$$2Ca_9HPO_4(PO_4)_5OH + H_2O \quad (2b)$$

Since the original work by Brown and Chow, the formation of HAp from a variety of particulate calcium phosphate-based reactants has been demonstrated. Included are acid−base reactions in which the acidic constituent is monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2\cdot H_2O$)[16] as shown in eq 3 and hydrolysis reactions in which α-tricalcium phosphate (α-$Ca_3(PO_4)_2$, α-TCP) converts to HAp as shown in eq 4. HAp formation from these compounds has been investigated:[17−19]

$$Ca(H_2PO_4)_2\cdot H_2O + 2Ca_4(PO_4)_2O \xrightarrow{H_2O}$$
$$Ca_9HPO_4(PO_4)_5OH + 2H_2O \quad (3)$$

$$3\alpha\text{-}Ca_3(PO_4)_2 + H_2O \xrightarrow{H_2O} Ca_9HPO_4(PO_4)_5OH \quad (4)$$

Each of these reactions is exothermic; however, systematic characterization of their energetics has not been carried out. Such determinations are important because the extents of these

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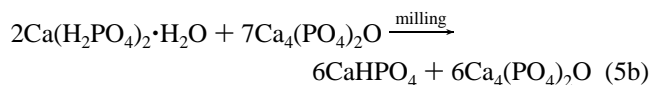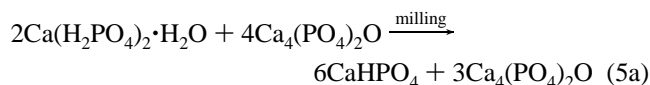[‡] Current affiliation: Framatron Inc, York, PA.

reactions need to be determined depending on the presence of electrolytes and proteins found in biological fluids. This knowledge is critical if HAp is to be formed in vivo using calcium phosphate precursors. It is the primary purpose of this paper to establish the enthalpies of formation of biologically relevant calcium phosphates in water.

2. Experimental Section

2.1. Precursor Preparation. Three chemical systems will be discussed: in *chemical system 1*, $CaHPO_4$ and $Ca_4(PO_4)_2O$ react to form SHAp and CDHAp; in *chemical system 2*, $CaHPO_4 \cdot 2H_2O$ and $Ca_4(PO_4)_2O$ react to form SHAp and CDHAp; in *chemical system 3*, α-$Ca_3(PO_4)_2$ hydrolyzes to form CDHAp.

Chemical System 1. $Ca_4(PO_4)_2O$ was synthesized by reacting an equimolar mixture of particulate $CaCO_3$ and $CaHPO_4$ (Fisher Scientific Co.). The reactants were milled in ethanol on a vibratory mill for 36 h to attain a particle size of a few micrometers. After removal of the ethanol by filtration and evaporation, the mixture was fired at 1400 °C for 4 h to produce $Ca_4(PO_4)_2O$. In a prior investigation concerning its hydrolysis, $Ca_4(PO_4)_2O$ synthesis is fully described.[20] The solid-state reactions of $CaHPO_4$ and $CaCO_3$ to synthesize $Ca_4(PO_4)_2O$ have also been studied in detail by Ciesla and Rudnicki.[21-24] Particulate $Ca(H_2PO_4)_2 \cdot H_2O$ (Baker) was reacted with $Ca_4(PO_4)_2O$ by vibratory comminution. The heterogeneous particles comprised of $Ca_4(PO_4)_2O$ and $CaHPO_4$ were synthesized by the following mechanochemical reactions:[14]

$$2Ca(H_2PO_4)_2 \cdot H_2O + 4Ca_4(PO_4)_2O \xrightarrow{\text{milling}}$$
$$6CaHPO_4 + 3Ca_4(PO_4)_2O \quad (5a)$$

$$2Ca(H_2PO_4)_2 \cdot H_2O + 7Ca_4(PO_4)_2O \xrightarrow{\text{milling}}$$
$$6CaHPO_4 + 6Ca_4(PO_4)_2O \quad (5b)$$

The Ca/P ratios of the precursors were prescribed to form either CDHAp or SHAp. These heterogeneous particles reacted according to eqs 2a and 2b to form HAp.

Chemical System 2. $Ca_4(PO_4)_2O$ was prepared as described above. $CaHPO_4 \cdot 2H_2O$ was precipitated by acid−base reaction of $Ca(H_2PO_4)_2 \cdot H_2O$ (Baker) and $Ca(OH)_2$. $CaCO_3$ was calcined at 1100 °C for 3 h. After cooling, the CaO that had formed was shaken in water for 30 min using a vibratory mill to produce $Ca(OH)_2$. This $Ca(OH)_2$ was added to a slurry of $Ca(H_2PO_4)_2 \cdot H_2O$ crystallites over a period of approximately 30 min. The $CaHPO_4 \cdot 2H_2O$ that formed was dried and interground with $Ca_4(PO_4)_2O$ to achieve an intimate physical mixture.[15] Samples were prepared to attain bulk Ca/P ratios of 1.5 and 1.67. These were reacted with water according to eqs 1a and 1b.

Chemical System 3. The α-$Ca_3(PO_4)_2$ powder was synthesized by a solid-state reaction in which equimolar proportions of $CaCO_3$ and calcium pyrophosphate ($Ca_2P_2O_7$) were fired for 4 h at 1150 °C. The product was vibratory milled for 24 h to produce a powder having a particle size of approximately 2.0 μm.[19] α-$Ca_3(PO_4)_2$ hydrolyzes to CDHAp according to eq 4.

2.2. Isothermal Calorimetry. The rates and extents of heat evolution during the formation of hydroxyapatite from chemical systems 1, 2, and 3 were determined by reacting the precursor solid(s) with water in an isothermal calorimeter using a water to solids weight ratio of 1:1. The isothermal calorimetry technique measured heat evolution as HAp formed according to the reactions summarized in eqs 1−4. Although the heat evolution data were collected at temperatures ranging from 15
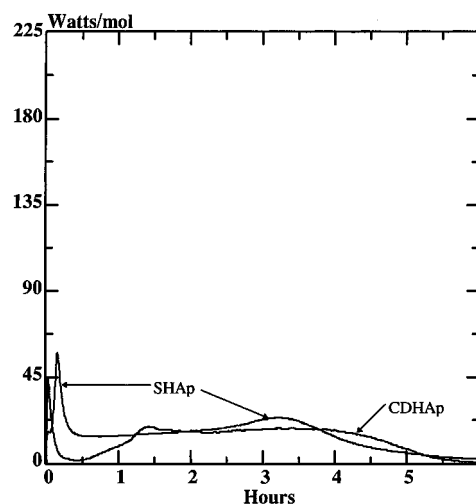

Figure 1. Comparison of heat evolution during CDHAp or SHAp formation from acid−base reactions involving $Ca_4(PO_4)_2O$ and $CaHPO_4$ (chemical system 1) at 37.4 °C.

to 70 °C, the bulk of the studies were carried out at 37.4 °C, physiological temperature.

Water in a syringe is thermally equilibrated to the same temperature as that of the powdered reactants. The latter are contained in an Au plated, Cu calorimeter cup that is surrounded by bismuth telluride thermopiles. The thermopiles are, in turn, in thermal contact with the body of the calorimeter. Constant temperature (± 0.01 °C) is maintained by thermal equilibration with a water bath. When water is inoculated into the powder, heat evolution initiates. Heat is recorded as a voltage output across the thermopiles, is digitized, and is stored on a microcomputer. By suitable calibration techniques, this voltage output is converted to a thermal output. Total enthalpy of reaction (ΔH_r) is calculated by numeric integration of the heat evolution data using Simpson's trapezoid rule. The calorimeter system used has been described in prior publications.[25,26] When further heat evolution could not be detected from a sample, the solids present were analyzed by X-ray diffraction to confirm that phase pure HAp had formed. The calorimeter constant, the ratio of thermal input per emf output, was periodically determined and was observed to remain constant to within 0.01% over the duration of the studies.

3. Results and Discussion

3.1. Kinetics. *3.1.1. Chemical System 1.* The rates of heat evolution during hydroxyapatite formation in chemical system 1 by the cohydrolysis of TetCP and DCP, eqs 2a and 2b, are shown in Figure 1. HAp formation is kinetically complex, and the variations in the rates of heat liberation with time result in three heat peaks. The kinetics of these reactions vary in response to the molar proportions of the reactants. The first heat peaks, which occur as the water and the solids are mixed, are of short duration. These "mixing peaks" are due to wetting and initial dissolution of the calcium phosphates. Mixing peaks are each followed by two reaction peaks. The area under the first reaction peak represents approximately 15% of the total heat evolved. Prior analysis [14] determined these to be associated with the nucleation and growth events, respectively, regardless of whether stoichiometric or calcium-deficient HAp is formed. X-ray diffraction analysis and solution chemical analysis confirmed that the reactants were consumed at nearly the same rates regardless of the hydroxyapatite composition.

3.1.2. Chemical System 2. In chemical system 2, $CaHPO_4 \cdot 2H_2O$ replaces the $CaHPO_4$ used in chemical system 1 as the

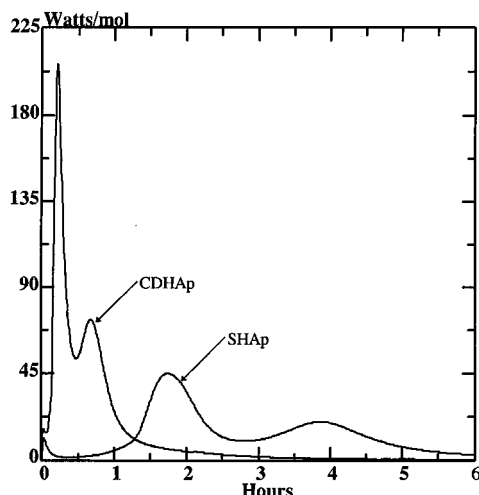Enthalpies of Formation in the P$_2$O$_5$−CaO−H$_2$O System

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Figure 2. Comparison of heat evolution during CDHAp or SHAp formation from acid−base reactions involving Ca$_4$(PO$_4$)$_2$O and CaHPO$_4$·2H$_2$O (chemical system 2) at 37.4 °C.

Figure 3. Heat evolution during the hydrolysis of α-Ca$_3$(PO$_4$)$_2$ (chemical system 3) at 55 °C.

Figure 4. Comparison of the development of the enthalpy-of-reaction ΔH_r during CDHAp or SHAp from acid−base reactions involving Ca$_4$(PO$_4$)$_2$O and either CaHPO$_4$ (chemical system 1) or CaHPO$_4$·2H$_2$O (chemical system 2) and the hydrolysis of α-Ca$_3$(PO$_4$)$_2$ (chemical system 3) at 55 °C.

acidic particulate reactant.[15] Figure 2 shows the rates of heat evolution as HAp forms at 37.4 °C in this system. As in chemical system 1, two reaction peaks occur in the rate curves after a mixing peak. However, HAp formation from these reactants is mechanistically distinct from that formed in chemical system 1. In chemical system 2 Ca$_4$(PO$_4$)$_2$O is partially consumed while CaHPO$_4$·2H$_2$O is completely consumed, resulting in the formation of HAp of uncertain composition and an amorphous calcium phosphate (ACP) intermediate. Subsequently, these solids continue to react with the eventual disappearance of ACP and Ca$_4$(PO$_4$)$_2$O and the formation of CDHAp and SHAp. These mechanistic differences may be due in part to the preparative techniques used for each chemical system. In chemical system 2, CaHPO$_4$·2H$_2$O is precipitated as thin, platelike crystallites (>1 μm) and then milled with Ca$_4$-(PO$_4$)$_2$O. During milling the CaHPO$_4$·2H$_2$O is comminuted. In chemical system 1 the CaHPO$_4$ forms in association with the Ca$_4$(PO$_4$)$_2$O surfaces during a mechanochemical reaction. The hydrolysis of CaHPO$_4$·2H$_2$O dominates the kinetics in chemical system 2, while the intimacy of association between CaHPO$_4$ and Ca$_4$(PO$_4$)$_2$O in chemical system 1 balances their dissolution rates so that processes involved in hydroxyapatite nucleation and growth are the apparent rate-limiting mechanisms.

3.1.3. Chemical System 3. Figure 3 shows the rate heat evolution as a result of the hydrolysis of α-Ca$_3$(PO$_4$)$_2$ at 37.4 °C.[19] Only calcium-deficient HAp can be formed as a result of α-Ca$_3$(PO$_4$)$_2$ in the absence of a secondary source of calcium. Although chemical system 3 forms HAp from a single solid, heat peaks typical of HAp formation from calcium phosphate precursors are again observed. As in chemical system 2, the second calorimetric peak is associated primarily with the formation of HAp nuclei although some HAp growth is also associated with this peak. As the nucleation phenomena reach completion, the rate of heat evolution associated with the second peak rapidly decreases. The third calorimetric peak is the result of HAp growth.

Integration of the rate data shown in Figures 1−3 permits the determination of the total extents of heat evolution as these reactants convert to HAp. These data are shown in Figure 4, which compares the total heats evolved in the three chemical systems at 37.4 °C. Although the data presented are limited to physiological temperature, calorimetric curves were obtained at a variety of temperatures. (30−70 °C for chemical system 1; 15−70 °C for chemical system 2; 30−75 °C for chemical
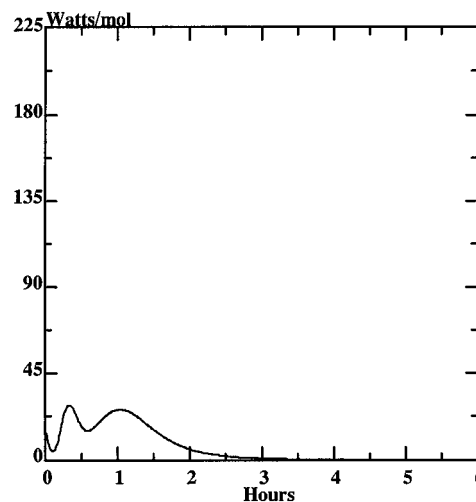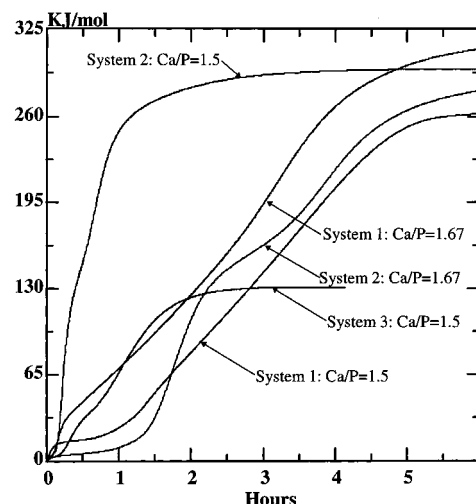
system 3). Except for those instances where reaction did not reach completion as confirmed by X-ray diffraction analysis of the solids, differences in the extent of heat evolution over these ranges of temperature were negligible. This indicates the enthalpy of formation values obtained can be treated as constants over these temperature ranges.

3.2. Hess' Law Calculations. Hydroxyapatite exhibits low solubility products, K_{sp} ∼10^{-85} M[16] for calcium-deficient[27] and ∼10^{-117} M[18] for stoichiometric HAp.[28] Because of this, enthalpies of formation of complex solutions were not considered. In the Hess' law analysis, the enthalpy of formation of water was assumed for the solutions remaining after complete reaction in these chemical systems. As the enthalpy of reaction (ΔH_r) data in Figure 4 show, reactions in chemical system 1 produced a total enthalpy of reaction (ΔH_r) of −261 and −320 kJ/mol for the formation of Ca$_9$HPO$_4$(PO$_4$)$_5$OH and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, respectively. The same hydroxyapatite compositions, when formed in chemical system 2, produced a total enthalpy of reaction (ΔH_r) of −240 and −295 kJ/mol, respectively. The formation of Ca$_9$HPO$_4$(PO$_4$)$_5$OH in chemical system 3 produced a ΔH_r of −133 kJ/mol. The enthalpies of formation ΔH_f for H$_2$O, CaHPO$_4$, CaHPO$_4$·2H$_2$O, and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ are known.[29,30]
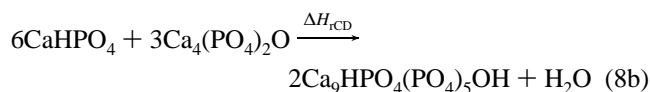
3.2.1. Chemical System 1. For CDHAp to be transformed to SHAp, it would need to react with a mole of CaO according to the following equation:
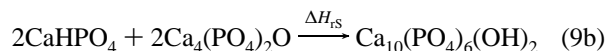
$$Ca_9HPO_4(PO_4)_5OH + CaO \xrightarrow{\Delta H_t} Ca_{10}(PO_4)_6(OH)_2 \quad (7)$$
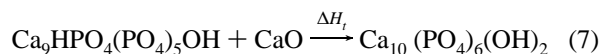
On the basis of the results obtained from isothermal calorimetry, thermodynamic analysis of the enthalpies of reaction ΔH_r and enthalpies of formation ΔH_f can now be considered.

Using Hess's law of heat summation eqs 2a, 2b, and 7 can be rewritten in terms of the enthalpies of formation (ΔH_f) of the reactants and products and the experimental enthalpies of reaction (ΔH_r):
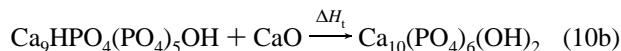
$$6\Delta H_{DCP} + 3\Delta H_{TetCP} + 2(-261_{.3} \text{ kJ/mol}) = $$
$$2\Delta H_{CDHAp} + \Delta H_{H_2O} \quad (8a)$$

$$6CaHPO_4 + 3Ca_4(PO_4)_2O \xrightarrow{\Delta H_{rCD}}$$
$$2Ca_9HPO_4(PO_4)_5OH + H_2O \quad (8b)$$

$$2\Delta H_{DCP} + 2\Delta H_{TetCP} + (-320_{.0} \text{ kJ/mol}) = \Delta H_{SHAp} \quad (9a)$$

$$2CaHPO_4 + 2Ca_4(PO_4)_2O \xrightarrow{\Delta H_{rS}} Ca_{10}(PO_4)_6(OH)_2 \quad (9b)$$

$$\Delta H_{CDHAp} + \Delta H_{CaO} + \Delta H_t = \Delta H_{SHAp} \quad (10a)$$

$$Ca_9HPO_4(PO_4)_5OH + CaO \xrightarrow{\Delta H_t} Ca_{10}(PO_4)_6(OH)_2 \quad (10b)$$

Values for the enthalpies of formation of $CaHPO_4$, CaO, and H_2O are $-181_{.4.4}$, $-635_{.2}$, and $-285_{.3}$, respectively.[30] Replacing the ΔH_f's with known values, eqs 8a, 9a, and 10a reduce to

$$3\Delta H_{TetCP} = 2\Delta H_{CDHAp} + 111_{23.1} \quad (11a)$$

$$2\Delta H_{TetCP} = \Delta H_{SHAp} + 394_{8.8} \quad (11b)$$

$$\Delta H_{CDHAp} = \Delta H_{SHAp} - \Delta H_t + 635_{.1} \quad (11c)$$

The literature value for ΔH_{SHAp} is -134_{77} kJ/mol.[31] Using this value, eq 11 can be solved simultaneously by Cholesky factorization. The values obtained are
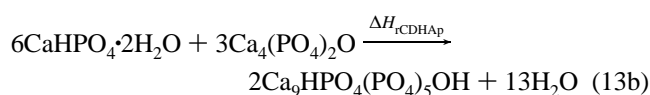
$$\Delta H_{TetCP} = -476_{4.1} \text{ kJ/mol} \quad (12a)$$

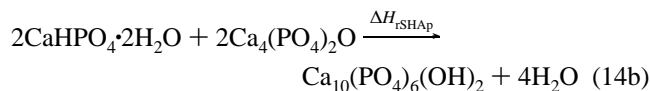$$\Delta H_{CDHAp} = -127_{07.7} \text{ kJ/mol} \quad (12b)$$

$$\Delta H_t = -134_{.2} \text{ kJ/mol} \quad (12c)$$

3.2.2. Chemical System 2. A similar heat summation can be performed on the reactions involving $CaHPO_4 \cdot 2H_2O$. The same unknowns, ΔH_{TetCP}, ΔH_{CDHAp}, and ΔH_t, apply, and they can be calculated from the set of equations in this system.

$$6\Delta H_{DCPD} + 3\Delta H_{TetCP} + 2(-240 \text{ kJ/mol}) = $$
$$2\Delta H_{CDHAp} + 13\Delta H_{H_2O} \quad (13a)$$

$$6CaHPO_4 \cdot 2H_2O + 3Ca_4(PO_4)_2O \xrightarrow{\Delta H_{rCDHAp}}$$
$$2Ca_9HPO_4(PO_4)_5OH + 13H_2O \quad (13b)$$

$$2\Delta H_{DCPD} + 2\Delta H_{TetCP} + (-295_{.0} \text{ kJ/mol}) = $$
$$\Delta H_{SHAp} + 4\Delta H_{H_2O} \quad (14a)$$

$$2CaHPO_4 \cdot 2H_2O + 2Ca_4(PO_4)_2O \xrightarrow{\Delta H_{rSHAp}}$$
$$Ca_{10}(PO_4)_6(OH)_2 + 4H_2O \quad (14b)$$

The value for the formation of $CaHPO_4 \cdot 2H_2O$ is $-240_{3.7}$ kJ/mol. Reusing eq 10a and replacing known values for variables to reduce eqs 13a and 14a, the following three equations can be solved simultaneously:

$$3\Delta H_{TetCP} = 2\Delta H_{CDHAp} + 111_{86.8} \quad (15a)$$

$$2\Delta H_{TetCP} = \Delta H_{SHAp} + 395_{9.2} \quad (15b)$$

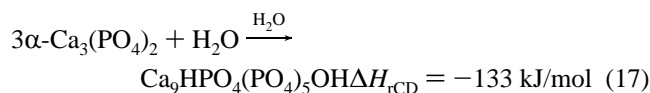$$\Delta H_{CDHAp} = \Delta H_{SHAp} - \Delta H_t + 635_{.1} \quad (15c)$$

The solved values according to this system are

$$\Delta H_{TetCP} = -475_{8.9} \text{ kJ/mol} \quad (16a)$$

$$\Delta H_{CDHAp} = -127_{31.75} \text{ kJ/mol} \quad (16b)$$

$$\Delta H_t = -134_{.2} \text{ kJ/mol} \quad (16c)$$

3.2.3. Chemical System 3. The enthalpy of reaction (ΔH_r) for α-$Ca_3(PO_4)_2$ is -133 kJ/mol of CDHAp formed.[19] The reaction consumes 1 mol of water for every 3 mol of α-$Ca_3(PO_4)_2$ hydrolyzed:

$$3\alpha\text{-}Ca_3(PO_4)_2 + H_2O \xrightarrow{H_2O}$$
$$Ca_9HPO_4(PO_4)_5OH \quad \Delta H_{rCD} = -133 \text{ kJ/mol} \quad (17)$$

For this reaction all enthalpies of formation values are known but Hess's law of heat summation is not met. Therefore, the enthalpy of formation ($\Delta H_{\alpha-TCP}$) of α-$Ca_3(PO_4)_2$ was recalculated from the relationship and the other enthalpies of formation.

$$\Delta H_{rCD} = \Delta H_{CDHAp} - (3\Delta H_{\alpha\text{-}TCP} + \Delta H_{H_2O}) = $$
$$-133 \text{ kJ/mol} \quad (18)$$

Solving for $\Delta H_{\alpha-TCP}$ produces a enthalpy of formation value of $-409_{6.5}$ kJ/mol for α-$Ca_3(PO_4)_2$. The magnitude of this value is 13 kJ/mol less than that previously reported.[30]

3.3. Comparison of the Three Systems. The enthalpy of formation values for the calcium phosphate phases are shown in Table 1. Using the results obtained from chemical systems 1 and 2, the enthalpy of formation (ΔH_f) for CDHAp is approximately 770 kJ/mol less than that of SHAp. This is consistent with the lower stability of CDHAp. Although the two systems shared the same variables, calculation of ΔH_f involved different equation sets. Despite this, the values for ΔH_{TetCP} differ only by about 0.11% between the two systems. The difference between the values for ΔH_{CDHAp} is 0.19%. Thus, these data are in close agreement despite the formation of CDHAp and SHAp by differing mechanistic paths using different calcium phosphate reactants that had been prepared in a variety of ways.

3.4. Thermodynamics Governing $Ca_4(PO_4)_2O$ Synthesis. Interest in forming hydroxyapatite at low temperature has generated considerable attention to the preparation of Ca_4-$(PO_4)_2O$. $Ca_4(PO_4)_2O$ is the only calcium phosphate more basic than $Ca_{10}(PO_4)_6(OH)_2$ and undergoes hydrolysis to form Ca_{10}-$(PO_4)_6(OH)_2$ and $Ca(OH)_2$.[20] In the polythermal P_2O_5−CaO binary system, $Ca_4(PO_4)_2O$ has a peritectic relationship with

Enthalpies of Formation in the $P_2O_5-CaO-H_2O$ System

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TABLE 1: Enthalpies of Formation of Compounds in the $P_2O_5-CaO-H_2O$ System[30,31]

formula		ΔH_f (kJ/mol)
$H_2O_{(l)}$		$-285._3$
$CaO_{(cr)}$		$-635._2$
$Ca(OH)_{2(cr)}$		$-986._1$
$H_3PO_{4(l)}$		$-126_{6.9}$
$CaHPO_{4(cr)}$		$-181_{4.4}$
$CaHPO_4 \cdot 2H_2O_{(cr)}$		$-240_{3.7}$
α-$Ca_3(PO_4)_{2(cr)}$		$-411_{0.0}$
	system 3	$-409_{6.5}$
$Ca_4(PO_4)_2O_{(cr)}$	system 1	$-476_{4.1}$
	system 2	$-475_{8.9}$
	average	$-476_{2.4}$
$Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O_{(cr)}$		
$Ca_9HPO_4(PO_4)_5OH_{(cr)}$	system 1	$-127_{07.7}$
	system 2	$-127_{31.7}$
	average	$-127_{19.7}$
$Ca_{10}(PO_4)_6(OH)_{2(cr)}$		$-134_{77.0}$

CaO.[32] As a liquid with a Ca/P ratio molar ratio of 2 is cooled, CaO crystallizes initially according to the reaction: $L \rightarrow L' + CaO$. At 1630 °C the peritectic relationship occurs: $L' + CaO \rightarrow Ca_4(PO_4)_2O$. Thus, phase pure $Ca_4(PO_4)_2O$ can be formed by solid-state reactions at temperatures from ~1300 to 1630 °C. Typically the reactants used are $CaHPO_4$ and $CaCO_3$. Thus

$$2CaHPO_4 + 2CaCO_3 \xrightarrow{\Delta H_r}$$
$$Ca_4(PO_4)_2O + H_2O(g) + 2CO_2(g) \quad (19)$$
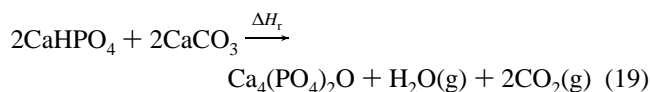
On the basis of the ΔH_f value determined for $Ca_4(PO_4)_2O$, the ΔH_r for the reaction shown by eq 19 becomes -259 kJ/mol.

It is not unusual that $Ca_{10}(PO_4)_6(OH)_2$ and CaO form as intermediates when $Ca_4(PO_4)_2O$ is synthesized according to eq 19 due to the water content of $CaHPO_4$. The presence of CaO and $Ca_{10}(PO_4)_6(OH)_2$ is often difficult to detect by X-ray diffraction analysis. However, subsequent acid−base reactions of $CaHPO_4$ or $CaHPO_4 \cdot 2H_2O$ with $Ca_4(PO_4)_2O$ coupled with the analysis of enthalpies of reaction can be used to confirm the phase purity of the $Ca_4(PO_4)_2O$.

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