

# Enthalpy of Formation and Mixing of Calcium-Cadmium Phosphoapatites

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## **Abstract**

*Calcium-Cadmium phosphoapatites solid solutions with formula  $Ca_{10-x}Cd_x(PO_4)_6Y_2$  where Y is OH, F, or Cl were synthesized and characterized by infrared spectroscopy, X Ray diffraction and chemical analysis. Using an isoperibol calorimeter the enthalpies of solution of these products in nitric acid 9 weight % have been determined. Thermochemical cycles were proposed to access to the enthalpies of formation and mixing. The results show an increase in the enthalpy of formation with the quantity of cadmium introduced in the lattice. The variations of the enthalpy of solution and the enthalpy of mixing versus Cd/(Ca+Cd) atomic ratio were correlated to the existence of two sites in the apatitic structure.*

## **INTRODUCTION**

Phosphoapatites form a large family of isomorphous compounds with the general formula  $Me_{10}(PO_4)Y_2$ , where Me is generally a divalent metal ( $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ) and  $Y^-$  a monovalent anion  $F^-$ ,  $Cl^-$  and  $OH^-$ . Generally, apatites crystallize in the hexagonal system space group  $P6_3/m$  [1]. The quasi compact arrangement of the phosphate group  $PO_4$  forms the skeleton of the structure and exhibits two types of sites. The first one is occupied by four Me cations placed on the ternary axis. They are called Me (I). The second site is occupied on its periphery by the other six Me cations called Me (II).

In spite of their natural abundance, thermochemical studies of phosphoapatites have not received much attention. This paper deals with the synthesis and characterization of solid solutions of calcium-cadmium fluor, hydroxy and chlorapatites and the determination of some of their thermochemical quantities.

## **SYNTHESIS AND CHARACTERISATION**

Calcium-cadmium hydroxyphosphoapatites (Ca-Cd/Hap) were synthesized by a double decomposition method [2] which consists in adding drop by drop for three hours a mixture of calcium and cadmium nitrates solution to a solution of diammonium phosphate previously heated to boiling. The pH of the two solutions is adjusted to about 9 by ammonia solution ( $d=0,92$ ). By varying the atomic Cd/Ca ratio in the nitrates solution, it is possible to obtain a continuous solid solution,  $Ca_{10-x}Cd_x(PO_4)_6(OH)_2$ , in the whole composition range ( $0 \leq x \leq 10$ ).

The same precipitation method has been used to prepare calcium-cadmium fluorapatites, (Ca-Cd/Fap) [3], the fluorine being introduced by dissolving ammonium fluoride in the diammonium phosphate solution. To obtain a stoichiometric product, the precipitate is ignited at  $600^\circ C$  under HF vapor resulting from the decomposition of ammonium fluoride which has

been placed in the furnace prior to the sample. With this method, it was possible to obtain solid solutions containing up to six cadmiums per unit cell, no more. The formula of Ca-Cd fluorapatite is  $\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6\text{F}_2$  with  $0 \leq x \leq 6$ . For chlorphosphoapatites solid solutions (Ca-Cd/Clap), The wet method described previously was unsuccessful and the synthesis was carried by using solid state [4] reaction between tricalcium phosphate (TriCa), tricalcium phosphate (TriCd) and cadmium chloride. By varying the atomic TriCa/TriCd in the reacting mixture one can prepare apatites containing 1 to 10 cadmium atoms per unit cell. This method consists in igniting the solid mixture in a sealed glass tube at about 550°C for 72 hours.

The purity of all these products was checked by X-Ray diffraction, IR spectroscopy and chemical analysis.

## CALORIMETRIC TECHNIQUE

The calorimeter used is an isoperibol one. It has been described previously in detail [5]. The measurement system consists of a thermistance probe of 2002  $\Omega$  at 25°C and a Wheatstone bridge. The thermistor is one of the four elements of the bridge. Joule effect is used to calibrate the calorimeter. The apparatus was tested by measuring the enthalpy of solution of trihydroxymethylamine (Tris) in 0.1 mol kg<sup>-1</sup> HCl aqueous solution. The deduced enthalpy (-29, 68 ± 0,08 kJ mol<sup>-1</sup>) is in good agreement with values found by Hill (-29,765±0,004) [6] and Vanderzee (-29,733±0,008) kJ mol<sup>-1</sup> [7].

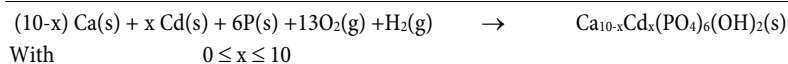
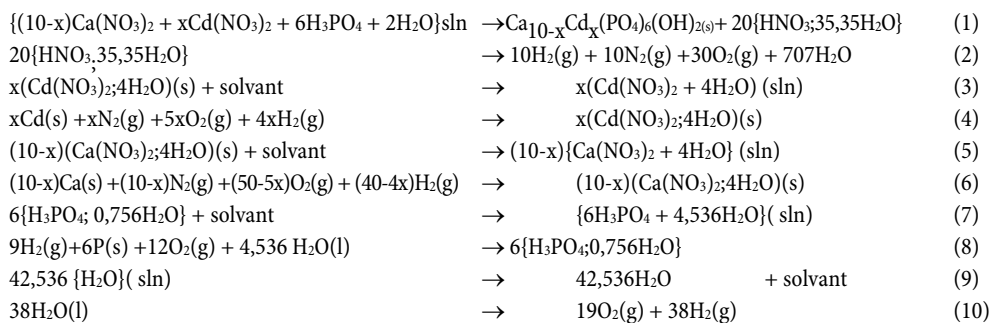
## ENTHALPY OF SOLUTION

Measurements of the enthalpies of solution of the studied phosphoapatites in 9 weight % nitric acid (1HNO<sub>3</sub>:35.35 H<sub>2</sub>O) were carried out as with the Tris in HCl. In the same volume of acid solution (350 cm<sup>3</sup>), different quantities of apatite were dissolved under stirring.

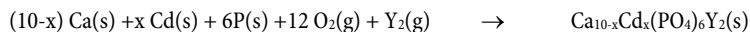
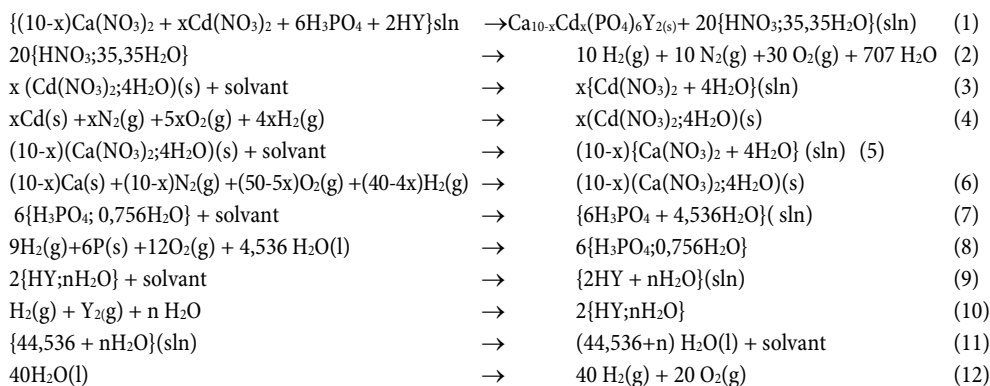
## ENTHALPY OF FORMATION

The direct measurement of the enthalpies of formation of these solid solutions is inaccessible. However it is possible to get this quantity by considering a thermochemical cycle involving a number of reactions. For these phosphoapatites we propose the following successions of steps, for which the "sum" corresponds to the enthalpy of formation of the studied product [8-10].

### For calcium-cadmium hydroxyapatites



## For calcium-cadmium halide phosphoapatites

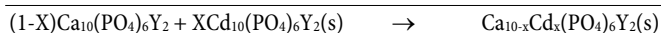
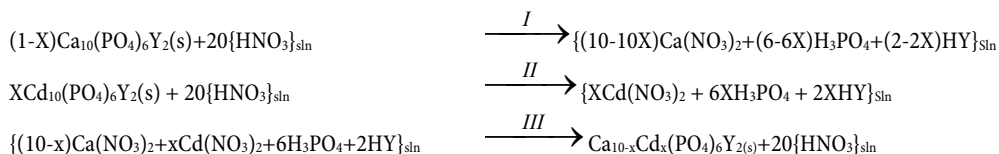


With:  $0 \leq x \leq 6$  for  $\text{Y} = \text{F}$  and  $n = 1,708$  (aqueous solution 40 weight % HF)  
and  $0 \leq x \leq 10$  for  $\text{Y} = \text{Cl}$  and  $n = 53,25$  (aqueous solution 37% weight % HCl)

One can notice that these successions of reactions involve several steps. Some of them are dissolution reaction or dilution processes (steps: 1, 3, 5, 7, 9, 11). Their corresponding enthalpies were measured according to the experimental procedure previously described. The others steps are formation reactions of well known compounds the corresponding enthalpies of which were taken from the literature [11].

## ENTHALPY OF MIXING

We can access to the thermal effect induced by the substitution of calcium by cadmium only in Ca-Cd/Hap and Ca-Cd/Clap solid solutions, by determining the enthalpy of mixing of the limit products. This quantity was deduced from the enthalpy of solution in the same solvent,  $\text{HNO}_3$  9 weight %, of the limit products and that of the corresponding solid solution. The reaction scheme succession leading to the enthalpy of mixing is as follows [10]:



With  $X = x/10$  and  $\text{Y} = \text{OH}$  or  $\text{Cl}$

The enthalpy of mixing is calculated according to the following relation:

$$\Delta_{\text{mix}}H = \Delta H(\text{I}) + \Delta H(\text{II}) + \Delta H(\text{III})$$

For Ca-Cd/Fap,  $\Delta_{\text{mix}}H$  can not be calculated because of the impossibility to synthesize the limit product,  $\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$ .

## RESULTS AND DISCUSSION

The values of the enthalpies of solution, formation and mixing for these phosphoapatites are gathered in tables 1, 2 and 3.

Table 1: Enthalpies of solution, formation and mixing of Ca-Cd/Hap

Formula	$\Delta_{\text{sol}}H^\circ(298\text{K})$ kJ mol <sup>-1</sup>	$\Delta_f H^\circ(298\text{K})$ kJ mol <sup>-1</sup>	$\Delta_{\text{mix}}H^\circ(298\text{K})$ kJ mol <sup>-1</sup>
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-365,7±1,7	-13305	0
Ca <sub>9,02</sub> Cd <sub>0,98</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-340,2±2,2	-12870	-19,9 ±3,9
Ca <sub>8,14</sub> Cd <sub>1,86</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-333,0±2,5	-12463	-22,1 ±4,3
Ca <sub>7,02</sub> Cd <sub>2,98</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-324,1±3,0	-11945	-24,6 ±4,9
Ca <sub>6,56</sub> Cd <sub>3,54</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-320,1±3,1	-11686	-29,1±5,1
Ca <sub>5,32</sub> Cd <sub>4,68</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-316,2±3,2	-11152	-22,8±5,1
Ca <sub>4,49</sub> Cd <sub>5,51</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-311,8±3,2	-10766	-22,5±5,2
Ca <sub>3,58</sub> Cd <sub>6,42</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-307,8±3,1	-10344	-21,3±5,3
Ca <sub>2,80</sub> Cd <sub>7,20</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-306,6±2,9	-9975	-18,1±5,2
Ca <sub>1,58</sub> Cd <sub>8,42</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-309,1±2,3	-9398	-8,6±5,1
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	-308,7 ± 2,3	-8652	0

Table 2: Enthalpies of solution and formation of Ca-Cd/Fap

Formula	$\Delta_{\text{sol}}H^\circ(298\text{K})$ kJ mol <sup>-1</sup>	$\Delta_f H^\circ(298\text{K})$ kJ mol <sup>-1</sup>
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	-197,3 ± 1,4	-13548
Ca <sub>9,0</sub> Cd <sub>0,99</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	-203,7 ± 1,7	-13083
Ca <sub>8,04</sub> Cd <sub>1,96</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	-209,5 ±1,2	-12610
Ca <sub>7,01</sub> Cd <sub>2,99</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	-213,7 ± 2,5	-12120
Ca <sub>6,03</sub> Cd <sub>3,97</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	-219,4 ± 2,2	-11672
Ca <sub>4,97</sub> Cd <sub>5,06</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	-217,5 ± 1,6	-11139
Ca <sub>4,06</sub> Cd <sub>5,94</sub> (PO <sub>4</sub> ) <sub>6</sub> F <sub>2</sub>	-211,8 ± 2,0	-10725

Table 3: Enthalpies of solution, formation and mixing of Ca-Cd/Clap

Formula	$\Delta_{\text{sol}}H^\circ(298\text{K})$ kJ mol <sup>-1</sup>	$\Delta_f H^\circ(298\text{K})$ kJ mol <sup>-1</sup>	$\Delta_{\text{mix}}H^\circ(298\text{K})$ kJ mol <sup>-1</sup>
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	*-313,4±1,3	*-13119	0
Ca <sub>9</sub> Cd <sub>1</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-316,3±2,8	-12645	8,1±4,1
Ca <sub>8</sub> Cd <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-318,4±2,1	-12172	15,5±3,4
Ca <sub>7</sub> Cd <sub>3</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-321,9±2,9	-11698	24,1±4,2
Ca <sub>6</sub> Cd <sub>4</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-322,4±3,1	-11227	29,7±4,3
Ca <sub>5</sub> Cd <sub>5</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-310,4±3,2	-10768	22,9±4,7
Ca <sub>4</sub> Cd <sub>6</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-303,4±2,4	-10304	21,1±3,6
Ca <sub>3</sub> Cd <sub>7</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-295,7±2,1	-9841	18,6±3,3
Ca <sub>2</sub> Cd <sub>8</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-284,1±3,2	-9382	12,4±4,4
Ca <sub>1</sub> Cd <sub>9</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-271,9±3,2	-8923	5,1±4,3
Cd <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> Cl <sub>2</sub>	-261,6±1,1	-8463	0

\*Taken from the literature [12]

Figures 1, 2, and 3, show the variation of the enthalpies of solution, formation and mixing versus the Cd/(Ca+Cd) atomic ratio, respectively.

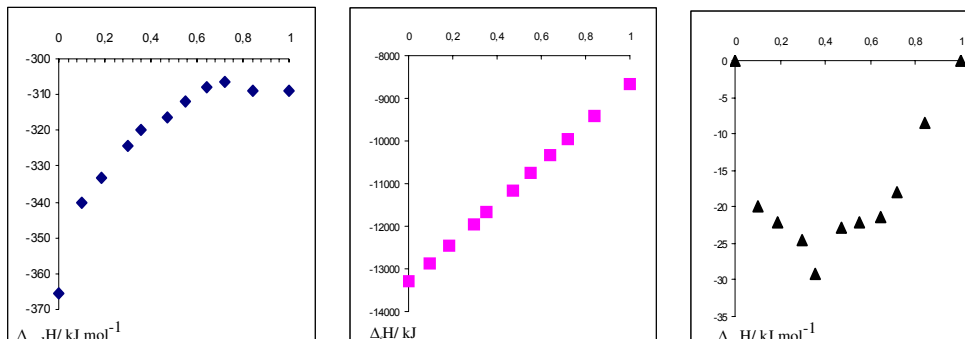


Figure 1: Enthalpy of solution, formation and mixing of Ca-Cd/OHapatites

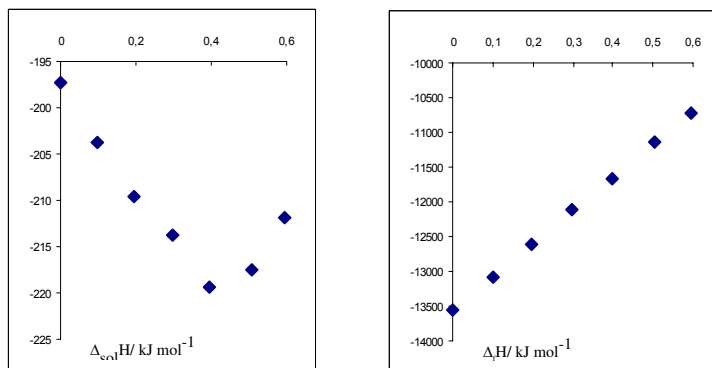


Figure 2: Enthalpy of solution and formation of Ca-Cd/Fapatites

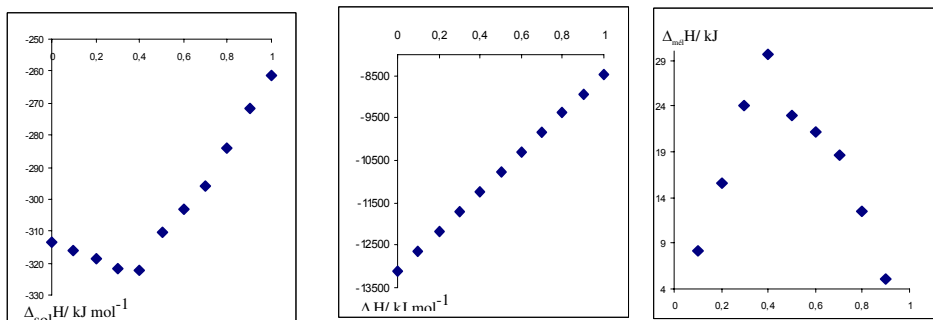


Figure 3: Enthalpy of solution, formation and mixing of Ca-Cd/Clapatites

One can notice a clear modification of the shape of the curves giving  $\Delta_{\text{sol}}H$  versus Cd/(Ca+Cd) ratio. This could be due to the preference occupancy of one of the sites in the apatite structure. For Ca-Cd/Hap, figure 1, an extremum is observed at about 0,85. Cristallographic study showed that cadmium substitutes preferentially to calcium in site II till Cd/ (Ca+Cd) = 0.9 [3]; above this ratio, substitution becomes statistical.

For Ca-Cd/Fap, figure 2, a minimum is observed for a composition near to 4 cadmium atoms per unit cell. It has been shown in this case that cadmium atoms occupy preferably site I [13]. Above this composition cadmium prefers site II. For Ca-Cd/Clap a minimum appears at about 0,4.

However, whatever is the anion Y, enthalpy of formation of these phosphoapatites increases with the quantity of cadmium introduced in the lattice, so introduction of cadmium contributes to the destabilization of the apatite structure. This result is in accordance with observation in thermal decomposition of these solid solutions: the higher the Cd content, the lower the decomposition temperature [2].

Finally enthalpy of mixing is positive for Ca-Cd/Clap and negative for Ca-Cd/Hap. This may be related to the difference of the structure of the limit product. Ca/Clap crystallizes in monoclinic system with space group  $P2_1/c$  whereas Cd/Clap crystallizes in hexagonal system with space group  $P6_3/m$ . In addition, one can notice a non symmetrical shape on the two curves. This may suggest that the required energy of substitution differs from one site to the other. It appears that cadmium substitution in the calcium apatites induces greater modifications in the lattice than substitution of the same amount of calcium in cadmium apatite.

## REFERENCES

- [1] K Sudasanan and R.A Young, *Acta Crystallogr. B* 25 8, 1534 (1969)
- [2] A. Nounah, S. Szilagyi, J.L. Lacout, *Ann. Chim. Fr* 10, 409 (1991)
- [3] A. Nounah, Thèse de Doctorat I.N.P Toulouse n° 577 (1992)
- [4] A. Ben Cherifa, Thèse de Doctorat d'Etat Université de Tunis II (2002)
- [5] A. Ben Cherifa, M. Jemal, *Ann. Chim. Fr*, 10, 543 (1985)
- [6] J.O. Hill, G. Ojelund, I. Wadsö, *J. Chem. Thermodyn*, 1, 111 (1969)
- [7] C.E. Vanderzee, D.H. Waugh, N.C. Haas, D.A. Wigg, *J. Chem. Thermodyn*, 12, 27 (1980)
- [8] A. Ben. Cherifa, A. Nounah, M. Jemal, J. L. Lacout, *Thermochim. Acta*, 237, 285 (1994)
- [9] A. Ben Cherifa, A. Nounah, J.L. Lacout, M. Jemal, *Thermochim. Acta*, 366, 7 (2001) [10] A. Ben Cherifa, M. Jemal, *J. Therm. Anal. Cal*, 68, 1035, (2002)
- [11] V.B. Parker, D.D. Wagman, W.H. Evans, Selected values of chemical thermodynamics properties, Technical note 270-6 NBS circular 500, Us Department of commerce, Table 94, (1971)
- [12] S.Somrani, Thèse de troisième Cycle, Université de Tunis II, (1991)
- [13] O.E Piro, M.C. Apella, E.J. Baran, B.E. Rivero, *Rev. Chim. Min*, 19, 11 (1982)