

## Enthalpy of formation and enthalpy of mixing of calcium and cadmium hydroxyapatites

A. Ben Cherifa<sup>a</sup>, M. Jemal<sup>a</sup>, A. Nounah<sup>b</sup> and J.L. Lacout<sup>b,\*</sup>

<sup>a</sup>*Faculte des Sciences, Département de Chimie, 1060 Tunis (Tunisia)*

<sup>b</sup>*Institut National Polytechnique de Toulouse, Ecole Nationale Supérieure de Chimie, Laboratoire des Matériaux, Physico-Chimie des Solides, U.R.A. C.N.R.S. no. 445-38, rue des 36 Ponts, 31400 Toulouse, France*

(Received 30 June 1993; accepted 9 November 1993)

### Abstract

Calcium–cadmium hydroxyapatite solid solutions with the general formula  $\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6(\text{OH})_2$  were prepared by a double decomposition method. The samples were characterized by X-ray diffraction, infrared spectroscopy and elemental analysis. Using an isoperibol calorimeter, enthalpies of solution of these products in 10% nitric acid solution were measured. The combination of these results with those of the limiting products  $x = 0$  and  $x = 10$  allows the determination of the enthalpies of mixing. Reaction schemes are proposed in order to determine the standard enthalpy of formation of cadmium and calcium hydroxyapatites.

### INTRODUCTION

Sedimentary phosphates make up 80% of the total production of phosphate minerals and provide the raw material for the phosphate fertilizer industry. They are generally phospho-calcium apatites containing traces of various elements. Among these, cadmium is a particularly toxic element, since it follows the food chain and becomes concentrated in the hard tissues of animals [1]. It may cause bone troubles such as “Itai-Itai” illness [2] or bone damage similar to osteoporosis [3]. It is estimated that 30–60% of the cadmium content in harvested crops comes from the atmosphere and the remainder from the soil [4]. The new standards set by the EEC countries limit the cadmium content for commercially produced phosphoric acid to less than 18 ppm [5, 6].

Synthesis of apatitic compounds containing cadmium allows the natural ores to be modelled, leading to a better understanding of their formation conditions as well as to the suggestion of possibilities for their evaluation.

---

\*Corresponding author.

Cadmium-containing apatites have already been prepared by some authors [7–9]; however, no work relating to solid solutions between calcium hydroxyapatite and cadmium hydroxyapatite or to their thermodynamic data has been reported. This paper deals with the dissolution enthalpies of cadmium–calcium hydroxyapatites and with the deduced mixing enthalpies of the limiting compounds.

#### EQUIPMENT AND METHODS

##### *Sample synthesis and characterization*

Calcium–cadmium hydroxyapatites were prepared in aqueous medium by a double decomposition method [10]. The method consists in adding dropwise a mixture of cadmium nitrate and calcium nitrate solutions (1 l; 0.2 M) for 3 h to a solution of diammonium phosphate (0.6 l; 0.2 M) previously heated to boiling. The pH of the two solutions was adjusted to  $\approx 9$  by the addition of ammonia solution ( $d = 0.92$ ). By varying the atomic Cd/Ca ratio of the nitrate solution, it was possible to change the composition of the solid obtained up to pure cadmium hydroxyapatite  $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$ . This latter compound was also prepared in caustic soda medium; in this case, the cadmium nitrate solution (1 l; 0.2 M) at pH = 4.5 and the caustic soda solution (1 l; 0.024 M) at pH = 12.3 were introduced dropwise, simultaneously and separately, into the phosphate solution (0.6 l; 0.2 M) at pH = 11. The solid was matured at boiling point and refluxed for 1 h in the mother solution, and was then filtered off and dried at 80°C for 15 h. Finally, samples were treated at 600°C for 1 h under  $\text{H}_2\text{O}$  vapour.

The products were characterized by X-ray diffraction using a CPS 120 INEL diffractometer and by infrared absorption spectroscopy between 4000 and 400  $\text{cm}^{-1}$  using a Perkin-Elmer 7700 FT-IR spectrometer. The calcium and cadmium contents were determined using atomic absorption and phosphorus was determined by colorimetry using the method of Gee and Deitz [11].

X-ray diffraction showed that all the samples were pure apatitic phases and crystallized in the hexagonal system  $P6_{3/m}$ . The infrared spectra were characteristic of hydroxyapatite. The bands in the ranges 3575–3530  $\text{cm}^{-1}$  and 750–620  $\text{cm}^{-1}$  due to  $\text{OH}^-$  ions could be noted. The experimental (Ca + Cd)/P atomic ratios of the samples were close to the stoichiometric value of 1.667.

Figure 1 shows the variation of the lattice parameters and lattice volume versus Cd composition. The simultaneous and continuous decrease of the lattice constants shows the progressive substitution of cadmium by calcium over the whole compositional range. The linear variation of the parameters follows a typical Vegard law and corresponds to the formation of a continuous solid solution between the two extremes: calcium ( $x = 0$ ) and cadmium ( $x = 10$ ) hydroxyapatites.

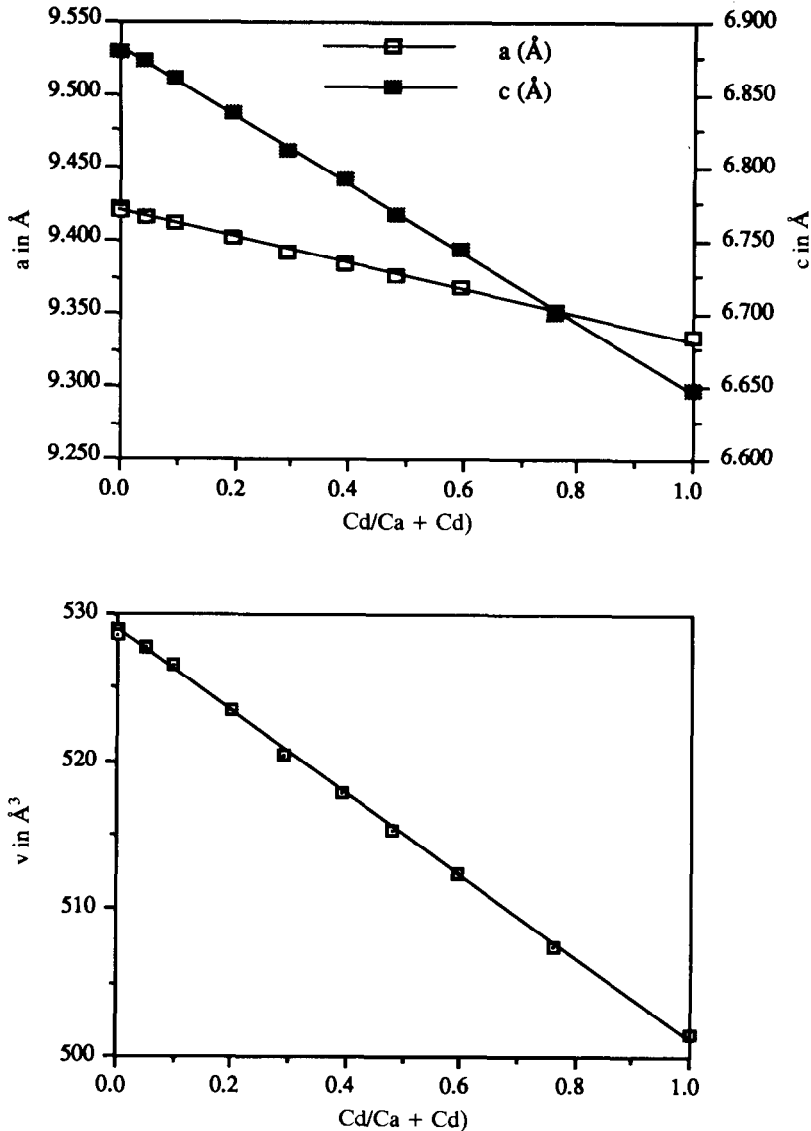


Fig. 1. Lattice constants of cadmium-calcium hydroxyapatite solid solutions versus the atomic ratio  $\text{Cd}/(\text{Ca} + \text{Cd})$ .

### Calorimeter apparatus

The apparatus used was an isoperibol calorimeter, and has been described previously in detail [12]. The measurement system consists of a precision thermistor of resistance  $2002 \Omega$  at  $25^\circ\text{C}$  and a Wheatstone bridge. The thermistor is one of the four elements of the bridge. The joule effect was used to calibrate the calorimeter. The apparatus was tested by measuring the enthalpy of the dissolution reaction of trihydroxymethylamine (Tris) in

TABLE 1

Enthalpies of calcium–cadmium hydroxyapatite solutions in 10% nitric acid

$X = x/10$	$\Delta H_{\text{diss}}/\text{kJ mol}^{-1}$	$X = x/10$	$\Delta H_{\text{diss}}/\text{kJ mol}^{-1}$
0.000	$-364.75 \pm 1.72$	0.551	$-311.79 \pm 3.23$
0.098	$-340.18 \pm 2.22$	0.642	$-307.81 \pm 3.10$
0.186	$-332.98 \pm 2.52$	0.720	$-306.60 \pm 3.48$
0.298	$-324.06 \pm 2.98$	0.842	$-309.11 \pm 2.89$
0.354	$-320.08 \pm 3.14$	1.000	$-308.69 \pm 2.31$
0.468	$-316.19 \pm 3.27$		

0.1 M  $\text{kg}^{-1}$  HCl aqueous solution (eight runs with specimens weighing from 40 to 200 mg accurately measured). The results were processed by a statistical method introduced by Sand [13]. The deduced enthalpy of  $-29.60 \pm 0.16 \text{ kJ mol}^{-1}$  is in agreement with values found by other authors:  $-29.764 \pm 0.009$  [14] and  $-29.793 \pm 0.009$  [15].

## RESULTS AND DISCUSSION

### *Solution enthalpy*

Measurement of the enthalpy of solutions of phosphates  $\text{Ca}_{10-x}\text{Cd}_x(\text{PO}_4)_6(\text{OH})_2$  in a 10% w/w nitric acid solution was carried out by the same method as that used with Tris. Quantities of each examined product (50–300 mg) were progressively dissolved in 350 ml of acid solution. The results are shown in Table 1.

The solution enthalpy of cadmium hydroxyapatite prepared in caustic soda medium was also determined; its value was  $-316.19 \pm 1.76 \text{ kJ mol}^{-1}$ .

### *Formation enthalpies*

The mass of the dissolved solid was very low, so dissolution was carried out in a large excess (about 40-fold) of acid compared with the stoichiometric amount. Thus the pH of the solution, which was very low ( $\approx 0$ ), did not undergo any measurable variation. Taking into consideration these factors and the distribution diagram of the entities  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  versus the pH [16], it can be concluded that in these experimental conditions only the entity  $\text{H}_3\text{PO}_4$  deserves attention, and we can propose the following reaction schemes for dissolution:



with  $\text{sln} = \text{HNO}_3 \cdot 35.35\text{H}_2\text{O}$ .

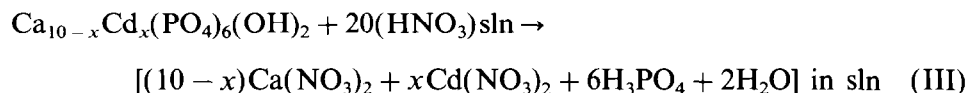
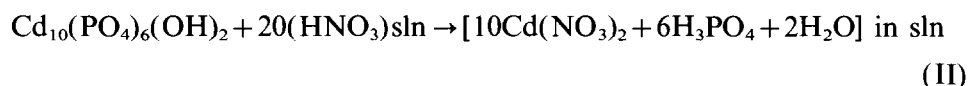
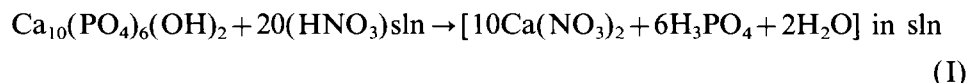
It can be noted that this succession of reactions consists of several steps; some of them are dissolution reactions (steps I and III) or mixing or dilution processes (steps VI and VIII). Their corresponding enthalpies were measured according to the experimental procedure previously described and the results are shown in Table 2.

The other steps are the formation reactions of well known compounds, and the corresponding enthalpies can be found in the literature (Table 3).

TABLE 2

Standard heat of solution in 10% nitric acid

	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{H}_3\text{PO}_4 \cdot 0.756\text{H}_2\text{O}$	$\text{H}_2\text{O}$
$\Delta H/\text{kJ mol}^{-1}$	$21.56 \pm 0.26$	$-7.87 \pm 0.04$	0



The determination of the standard enthalpy of formation for the limiting apatites was carried out by a succession of reactions, the sum of which is the formation reaction of the examined product. Thus, for cadmium hydroxyapatite  $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$  we can propose the following sequence:

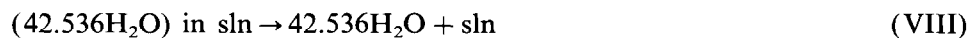
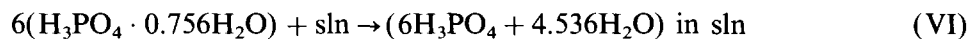
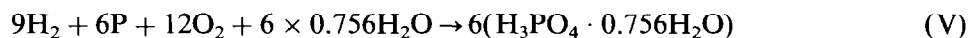
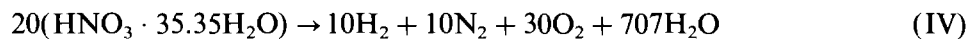
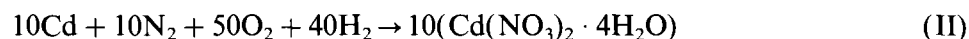
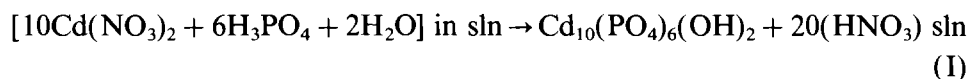


TABLE 3

Standard enthalpies of formation [17]

	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{H}_3\text{PO}_4 \cdot 0.756\text{H}_2\text{O}$	$\text{HNO}_3 \cdot 35.35\text{H}_2\text{O}$	$\text{H}_2\text{O}$
$\Delta H_{f298\text{K}} / \text{kJ mol}^{-1}$	-1650.06	-1272.70	-206.95	-286.00

From these data it is possible to determine the standard formation enthalpy for cadmium hydroxyapatite  $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$  prepared in an ammonium medium. The value obtained,  $\Delta H_f = -8652.65 \text{ kJ mol}^{-1}$ , is very close to the value for cadmium hydroxyapatite prepared in a soda medium,  $\Delta H_f = -8644.70 \text{ kJ mol}^{-1}$ . For calcium hydroxyapatite the standard formation enthalpy ( $-13313.61 \text{ kJ mol}^{-1}$ ) was determined in previous work [18].

#### Enthalpy of mixing

The enthalpy of mixing of the limiting products was determined by combining the solution enthalpies of solid solutions and those of the limiting products, according to the expression

$$\Delta H_m = (1 - X)\Delta H_I + X\Delta H_{II} - \Delta H_{III} \quad X = x/10$$

The values obtained are reported in Table 4.

Figure 2 shows the variation of the mixing enthalpy  $\Delta H_m$  versus the cadmium content  $X$ . However, it should be noted that this calculation was carried out using the value determined for the cadmium apatite prepared in ammonium medium.

#### DISCUSSION AND INTERPRETATION

The mixing enthalpy and the dissolution enthalpy curves respectively present a minimum close to 0.4 and a maximum close to 0.6 (Fig. 3). This

TABLE 4

Enthalpies of mixing

$X = x/10$	$\Delta H_m / \text{kJ mol}^{-1}$	$X = x/10$	$\Delta H_m / \text{kJ mol}^{-1}$
0.000	0.00	0.551	-22.06
0.098	-19.47	0.642	-20.93
0.186	-21.35	0.720	-17.79
0.298	-23.95	0.842	-8.46
0.354	-24.83	1.000	0.00
0.468	-22.32		

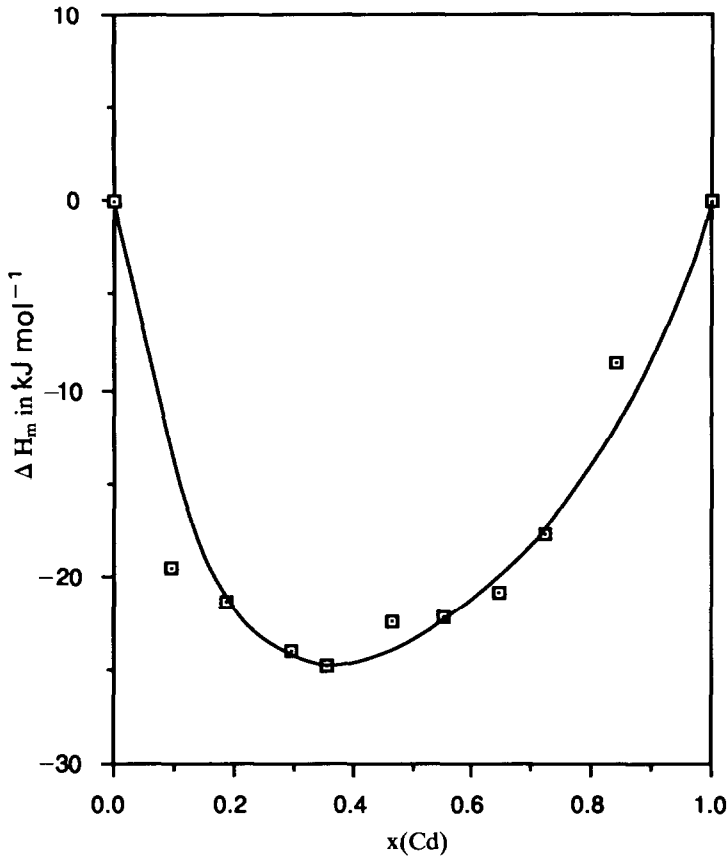


Fig. 2. Variation of the enthalpy of mixing versus the composition of cadmium–calcium hydroxyapatite.

is probably related to the existence, in the hexagonal apatite structure, of two types of cationic sites:  $M_I$  sites, of which there are four situated on the tertiary axes at the half height ( $c/2$ ) of the lattice, and  $M_{II}$  sites, of which there are six situated round the sixfold axis.

The extrema observed in enthalpies cannot be related to the progressive filling up of sites I and sites II; previous crystallographic studies [19] have shown that cadmium is located simultaneously at the two cationic sites with just a weak preference for sites II in hydroxyapatite. The non-symmetrical shape of  $\Delta H_m$  and  $\Delta H_{diss}$  may suggest that the required energy of substitution differs from one site to another. It appears that cadmium substitution in the calcium apatite induces greater modifications of the lattice and consequently of the lattice energy than substitution of the same amount of calcium in cadmium apatite. However, the formation enthalpy increases with the quantity of cadmium, so the introduction of cadmium contributes to the destabilisation of the structure: this is in agreement with the observa-

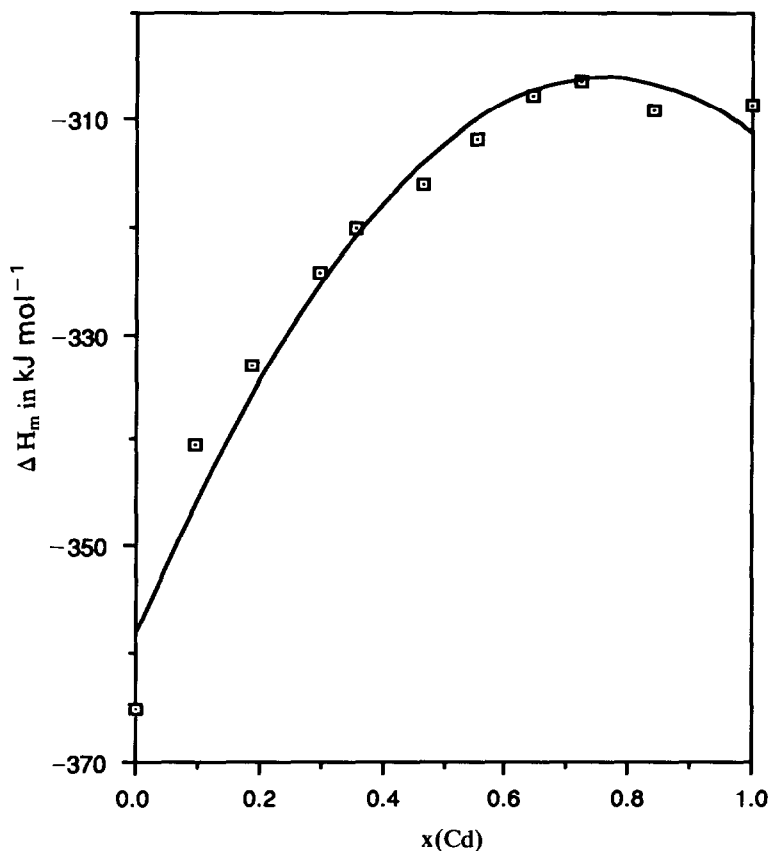


Fig 3. Variation of the enthalpy of dissolution versus the composition of calcium-cadmium hydroxyapatite.

tions on thermal decomposition of these products, i.e. the higher the Cd content, the lower the decomposition temperature [10].

One point should be stressed concerning the solution enthalpy of cadmium hydroxyapatite ( $x = 10$ ). As mentioned previously, this apatite was prepared using two different methods: in ammonium medium and in caustic soda medium, and the values obtained were respectively  $\Delta H = -308.69 \pm 2.31 \text{ kJ mol}^{-1}$  and  $-314.51 \pm 1.76 \text{ kJ mol}^{-1}$ . This slight discrepancy could be attributed to traces of sodium ions introduced into the crystallites or adsorbed at the surface.

#### REFERENCES

- 1 Cadmium in phosphates: one part of wider environmental problem, Phosphorus Potassium, 162 (1989) 23.
- 2 K. Tsuchiya, Keijo J. Med., 18 (1969) 181.
- 3 T. Ishida, Y. Ogawa, C. Yoshioka, T. Aoba, K. Hasegawa and T. Yagi, Osaka Daigaku, Shigaku Zasshi, 22 (1977) 275.



- 4 The Cadmium Question: A Survey, TECMIN, Paris, 1984.
- 5 Pollution of the Environment by Cadmium, COM (87) 165, Final Commission of the European Communities Brussels (21 April 1987).
- 6 Council resolution on a community action programme to combat environmental pollution by cadmium, 88/C30/01, Off. J. Eur. Communities, No. C30/1 (4 February 1988).
- 7 R.Z. Legeros, M.H. Taheri, G.B. Quirologoco and J.P. Legeros, Proc. Int. Congr. Phosphorus Compd., 2nd, 1980, April, Boston, MA, p. 89.
- 8 E.J. Baran and M.C. Apella, Rev. Chim. Miner., 16 (1979) 527.
- 9 W.E. Klee and G. Engel, J. Inorg. Nucl. Chem., 32 (1970) 1837.
- 10 A. Nounah, J.Szilagyi and J.L. Lacout, Ann. Chim. Fr., 15 (1990) 409.
- 11 A. Gee and V.R. Deitz, Anal. Chem., 25 (1953) 1320.
- 12 A. Bencherifa and M. Jemal, Ann. Chim. Fr., 10 (1985) 543.
- 13 D.E. Sand, J. Chem. Educ., 51 (7) (1974) 473.
- 14 J.O. Hill, G.O. Jelund and I. Wadsö, J. Chem. Thermodyn., 1 (1969) 118.
- 15 G.E. Vadergee, D.H. Wangh, N.C. Haas and D.A. Wigg, J. Chem. Thermodyn., 12 (1980) 27.
- 16 G. Dennis, M. Hayes and M. Hiefje, Chemical Separation and Measurement, Saunders Golden Sunburst Series, 1974.
- 17 B. Parker, D. Wagman and H. Evano, J. Res. Natl. Bur. Stand., 270 (1971) 6.
- 18 A. Bencherifa, S. Somrani and M. Jemal, J. Chim. Phys., 88 (1991) 1893.
- 19 A. Nounah, J.L. Lacout and J.M. Savariault, J. Alloys Compd., 188 (1992) 141.