



## Review

# A comprehensive guide to experimental and predicted thermodynamic properties of phosphate apatite minerals in view of applicative purposes



Christophe Drouet\*

CIRIMAT Carnot Institute, "Phosphates-Pharmacotechnics-Biomaterials" group, University of Toulouse, UMR CNRS/INPT/UPS 5085, Ensiacet, 4 allée Emile Monso, 31030 Toulouse cedex 4, France

## ARTICLE INFO

## Article history:

Received 21 January 2014

Received in revised form 22 September 2014

Accepted 26 September 2014

Available online 20 October 2014

## Keywords:

Apatite

Thermodynamic properties

Predictive methods

Additive model

VBT

Enthalpy

Gibbs free energy

Entropy

Periodic table of apatites

Stability

## ABSTRACT

Apatite minerals represent a major class of ionic compounds of interest to many disciplines including medical sciences, geology, anthropology, cosmology, environmental and nuclear sciences. Yet, these compounds have not received great attention from a thermodynamic viewpoint, and some diverging data – often drawn from molecular modeling assays – were reported. In this contribution, an extensive literature overview of available experimental-based data on  $M_{10}(PO_4)_6X_2$  apatites with  $M = Ca, Ba, Sr, Mg, Cd, Pb, Cu, Zn$  and  $X = OH, F, Cl$  or  $Br$  has first been made, on the basis of standard formation energetics ( $\Delta H_f^\circ$  and  $\Delta G_f^\circ$ ) as well as entropy  $S^\circ$  and molar heat capacity  $C_{p,m}^\circ$ . The case of oxyapatite was also included. From this overview, it was then possible to identify general tendencies, evidencing in particular the primary role of electronegativity and secondarily of ionic size. Using the experimental data as reference, several predictive thermodynamic methods were then evaluated, including the volume-based-thermodynamics (VBT) method and a more advanced additive contributive model. In particular, the latter allowed obtaining estimates of thermodynamic data of phosphate apatites within a maximum of 1% of relative error, generally within 0.5%. Fitted  $h_i$ ,  $g_i$  and  $s_i$  contributive parameters are given for bivalent cations and monovalent anions, so as to derive, by simple summation, coherent estimates of  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$  and  $S^\circ$  for any apatite composition, at  $T = 298$  K. The model was shown to also lead to consistent estimates in cases of solid-solutions or even non-stoichiometric or hydrated phosphates apatites. Ultimately, a *periodic table of recommended thermodynamic properties* of 33 phosphate apatites end-members (at  $T = 298$  K and 1 bar) was established, with the view to serve as an easily readable reference database.

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## 1. Introductory assessments

Phosphate-bearing apatites, for which stoichiometric end-members generally respond to the chemical formula  $M_{10}(PO_4)_6X_2$  ( $M$  and  $X$  representing respectively a divalent cation and a monovalent anion) constitute an important group of mineral compounds. Either found in Nature (bones and teeth [1], rocks and sediments [2,3]) or obtained by synthesis, these minerals are in particular well-known in various scientific communities including medical and biomaterials sciences (bone tissue engineering, nanomedicine) [1,4–6], anthropology [7–9], geology/mineralogy [2,3,10], or else environmental sciences (immobilization of phosphates and metallic compounds, nuclear sciences) [11], among other domains. If hydroxyapatite ( $Ca_{10}(PO_4)_6(OH)_2$ ) and fluorapatite ( $Ca_{10}(PO_4)_6F_2$ ) are probably the most illustrious examples in this series of compounds, chlorinated or bromated counterparts as well as apatites

containing other cations than calcium (such as cadmium, lead, magnesium, strontium...) are also encountered [12,13] and questions relating to their relative stability, solubility, etc. regularly arise. Besides, stoichiometric end-members are not the only phases of interest, especially when aqueous precipitation at moderate temperature is involved [5,14]: non-stoichiometric apatite compositions are generally obtained in such conditions (unless perhaps for very long periods of time), and their thermochemical features are bound to depart from those of their stoichiometric parent phase, as we showed recently in the case of biomimetic apatites [15].

Whether for applied considerations (for answering questions like: which phase is the most stable in given experimental conditions? which of the present or expected phases is the most soluble? can we expect to prepare and stabilize a given substituted apatite phase in given conditions?... ) or for more fundamental purposes, the need for reliable and readily usable thermodynamic data in terms of Gibbs free energies, enthalpies, entropies, or else heat capacities is obvious. Yet, regretfully, there is only a scarce literature addressing the thermodynamics of apatites.

\* Tel.: +33 534323411.

E-mail address: [Christophe.Drouet@ensiacet.fr](mailto:Christophe.Drouet@ensiacet.fr)

In this context, the goal of this paper is multiple. First, an overview of experimental-based reported thermochemical data for phosphate apatites will be listed, the idea being to gather the information dealing phosphate apatite minerals in a *single* document that could then serve as reference database in the future. Second, the use of various predictive methods for estimating thermodynamic data [16–19] – increasingly evoked in the literature for example for estimating data for not-yet synthesized materials or for cross-checking uncertain experimental data – will be investigated, with the final view to examine the case of solid-solutions or even non-stoichiometric compounds. Their application (for the first time with a specific focus on apatite minerals) will be evaluated and compared; and apatite-fitted parameters will then be determined. Finally, a comprehensive *periodic table of phosphate apatites recommended thermodynamic properties* will be established (in much the same way as was done for classifying not only chemical elements, but also other systems such as proteic structures [20] or also aminoacids [21]), so as to provide an easily-readable and portable chart, classified on the basis of apatite chemical composition.

This paper deals specifically with the wide family of phosphate apatites. Samples containing silicates, carbonates, arsenates or other molecular ions in place of phosphates are not addressed here; they will be the object of other dedicated studies. Throughout this contribution, formula units in the form  $M_{10}(PO_4)_6X_2$  will be used (rather than  $M_5(PO_4)_3X$ ) since it is more customary in nowadays studies. A total of 33 apatite end-member compositions involving various divalent  $M^{2+}$  ions and monovalent  $X^-$  anions will be examined in this work (including also the exceptional addition of calcium oxyapatite  $Ca_{10}(PO_4)_6O$  where  $2X^-$  are replaced by one  $O^{2-}$  ion).

## 2. Overview of experimental-based thermodynamic data on $M_{10}(PO_4)_6X_2$ apatites

Despite the vast scientific literature dealing with apatitic compounds (>15,800 entries in Web of Science® only for the last two decades) and the numerous multidisciplinary domains of research/applications where they may be involved, one can notice the relative scarcity of dedicated thermodynamic studies. In some instances, however, some data have been determined, and experimental-based evaluations were reported especially in terms of enthalpy measurements through calorimetry or dissolution experiments. Table 1 gathers the available thermodynamic data corresponding to the formation energetics of  $M_{10}(PO_4)_6X_2$  apatite compounds (at  $T = 298$  K and 1 bar). The case of oxyapatite  $Ca_{10}(PO_4)_6O$  (where  $O^{2-}$  replaces  $2X^-$ ) was also added since it represents another important apatitic compound. Some research groups such as Jemal *et al.* or Vieillard and Tardy have significantly contributed in this domain (see references for table 1). Published values for standard entropies  $S^\circ$  have also been included in this table, although they often arise from estimations rather than on actual experimental measurements [2,22] (e.g. considering in a first approximation the system as energetically equivalent to the sum of its constituting binary compounds [22]). Nonetheless entropy values are generally used, in practice, in conjunction with enthalpy with the final goal to determine standard Gibbs free energies  $\Delta G_f^\circ$  (which represent the actual “driving force” of a chemical process). Since such thermodynamic properties are generally given for the reference temperature of 298 K, the entropy term  $T\Delta S$  (in  $\text{kJ} \cdot \text{mol}^{-1}$ ) therefore gets multiplied by a factor 0.298. This then drastically limits the effects of entropy imprecision on the final evaluation of  $\Delta G_f^\circ$  which, for such complex oxide materials, have a clearly dominant enthalpy contribution (see table 1).

Some heat capacity values ( $C_{p,m}^\circ$ ), or their temperature coefficients in the function  $C_{p,m}^\circ = f(T)$ , have also been sporadically

reported. Table 2 summarizes the published data for phosphate-bearing apatites  $M_{10}(PO_4)_6X_2$  (as well as oxyapatite) along with the corresponding references. In the temperature ranges where the  $C_{p,m}^\circ = f(T)$  temperature functions are reported (indicated in table 2), these values may then allow one to evaluate  $\Delta H_f^\circ$  and  $S^\circ$  (and then  $\Delta G_f^\circ$ ) at any final temperature  $T_f > 298$  K thanks to the following equations:

$$\Delta H_f^\circ(T_f)/(\text{kJ} \cdot \text{mol}^{-1}) = \Delta H_f^\circ(298 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1}) + \int_{298}^{T_f} C_{p,m}^\circ/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})dT, \quad (1)$$

and

$$S^\circ(T_f)/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = S^\circ(298 \text{ K})/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + \int_{298}^{T_f} \frac{C_{p,m}^\circ/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})}{T/K}dT. \quad (2)$$

Data for temperatures lower than 298 K were only occasionally made available, especially for fluorapatite and chlorapatite [50]. It may be noted from table 2 that, at least at  $T = 298$  K, the  $C_{p,m}^\circ$  values for the apatites listed are rather similar, roughly in the range (700 to 800)  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  and with an average value at  $T = 298$  K close to 750  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ .

The literature data gathered in table 1 provide an overview of enthalpy, Gibbs free energy of formation and/or standard entropy of a variety of phosphate-bearing apatite compounds exhibiting different  $M^{2+}$  or  $X^-$  ionic contents (except in the case of oxyapatite where  $2X^-$  are replaced by one  $O^{2-}$  ion). The discrepancies observable in some cases probably arise from variable crystallinity states, polymorphs (either hexagonal or monoclinic, those not being systematically identified in literature reports), nonstoichiometry, hydration state and/or the presence of undetected impurities. A lower degree of crystallinity, for example, may favor the obtainment of somewhat less negative values [68]. Concerning polymorphism, in the case of apatites the difference between the hexagonal ( $P6_3/m$ ) and the monoclinic ( $P2_1/b$ ) symmetries lies in fact only in the positioning of the  $X^-$  anions along the apatitic channels (giving rise or not to a mirror plane) and does not correspond to a large ion rearrangement; therefore the energetics of formation are expected to not differ very significantly (although not being identical), which allows considering both polymorphs.

With this recapitulated overview of available data, it is then possible to detect more clearly some trends in terms of  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$  and/or  $S^\circ$ . For instance, for a given  $X^-$  anion (taken among  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$  or  $\text{Br}^-$ ), both  $\Delta H_f^\circ$  and  $\Delta G_f^\circ$  become significantly less negative (exothermic) when alkaline earth  $M^{2+}$  elements such as  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  or  $\text{Sr}^{2+}$  are replaced by heavy metal ions ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ) or by transition metals (such as  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$ ). It illustrates the direct impact of apatites composition on their formation energetics. It is however difficult, by the sole inspection of table 1, to draw more “advanced” conclusions. To do so, the data from table 1 were compared by plotting  $\Delta H_f^\circ$  or  $\Delta G_f^\circ$  as a function of specific characteristics of the ions involved. For example, the complete substitution of  $\text{Ca}^{2+}$  ions (ionic radius [69] 1.00 Å in coordination VI) by smaller  $\text{Cu}^{2+}$  (0.73 Å) or larger  $\text{Ba}^{2+}$  (1.36 Å) may be expected to lead to diversely stable systems. Also, replacing  $\text{OH}^-$  ions from hydroxyapatite by various halides is anticipated to produce significant changes in thermodynamic properties.

If the relative ion sizes probably come into play for modifying thermodynamic features, other parameters such as the affinity of the cation for oxygen or else the strength of M–O bonds may also be appropriately investigated. In this contribution, the potential correlation with six different parameters has been checked. The ionic radius (extracted from reference [69]) and the derived ionic volume were two parameters considered for examining the effect

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