

Thermochemistry and Relative Stability of Apatite Phosphates

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Abstract

Fluor- hydroxy- and chlor-apatites of Ca, Ba, Sr, Cd and Pb have been synthesized and characterized by X ray diffraction, IR spectroscopy and chemical analysis. They are dissolved in a nitric solution using an isoperibol calorimeter. Combining the dissolution results with other results obtained in the same device or picked from literature leads to the enthalpies of formation of these products. The relative stability of the products is first discussed by considering the enthalpies of formation. However, one can access to a more realistic stability scale by calculating the Gibbs energies of formation. This calculation is based on the involvement of the apatites in reactions for which the entropies of the reactants are tabulated. Ca fluor- and hydroxy-apatites are taken as examples, and the results show that P_4O_{10} reactional schemes could be considered to calculate $\Delta_r G^\circ(T_0)$ for all the products. This calculation leads to more realistic stability scale for the apatites.

INTRODUCTION

Thermodynamic stability of the compounds is often discussed on the basis of enthalpy of formation. This is because the entropy term is not easy to be determined in comparison to enthalpy, which is more easily accessible through calorimetric measurements.

For apatite phosphates, the first thermochemical data appeared in 1958¹. During the two following decades a few data have been published from time to time^{2,3,4}. This is probably because of the lack of systematic techniques of synthesis and characterization of this kind of products. In the beginning of 1980's some techniques have been settled up. Consequently, thermochemical data began to appear more frequently in literature.

Synthesis of apatite compounds has been carried out according to one of two main methods. The first one, called the wet method, consists in precipitating a solid phase from phosphoric solution $[(NH_4)_2HPO_4]$ into which a metal solution is added drop by drop. After ignition at high temperature, the solid leads to the apatite compound. The second method (a dry one) is based on the reaction between solid reactants at high temperature in a particular atmosphere. Between the ignition periods, the solid mixture is cooled and grinded in presence of acetone. All the products have been characterized by X ray diffraction, IR spectroscopy and chemical analysis. A particular attention has been placed on IR characterization because of its high sensitivity to detect unwanted entities in the solids, such as carbonate and pyrophosphate groups.

THERMOCHEMICAL DETERMINATIONS

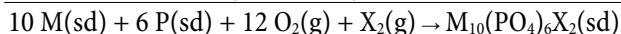
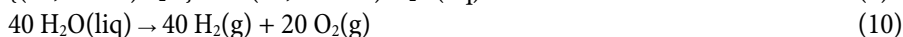
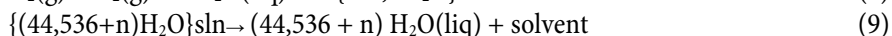
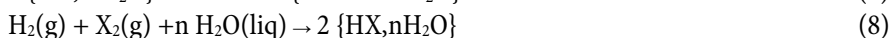
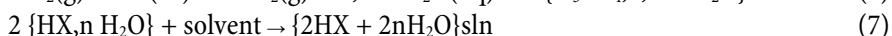
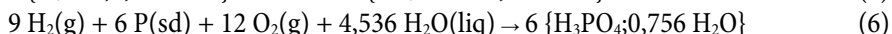
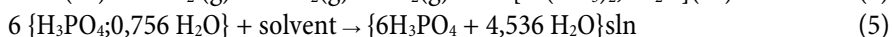
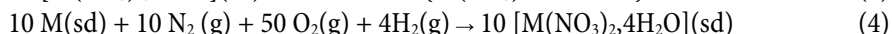
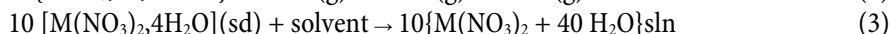
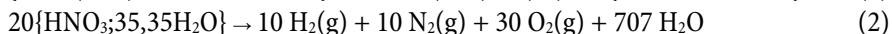
Enthalpy of solution

Various amounts of each product have been dissolved in 9% weight nitric acid solution (written as HNO_3 ; 35,35 H_2O) at 25°C , and the resulting enthalpies have been determined using an isoperibol calorimeter. The reaction occurs in a Dewar flask containing 350 ml of acid solution. The solid to be dissolved (or the liquid to be diluted) is deposited in a thin wall glass ball which is immersed in the liquid phase. The thermal process is started by breaking the ball and dispersing its content in the liquid. The device is provided with an axial stirrer and an electrical resistance connected to the units commonly used in such a technique. The device has been checked by a standard dissolution reaction.

Dissolution of various amounts of a solid in the same quantity of solution at atmospheric pressure and 25°C (T_0), leads to a mean value for the standard molar enthalpy of solution. However, the dissolved solid amounts are far less than the stoichiometric quantities and the solution keeps a very low value of pH. Consequently, the main entity present in the medium is H_3PO_4 .

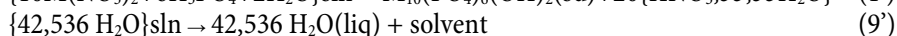
Enthalpy of formation

In order to access to the enthalpy of formation of the apatite, one has to imagine a succession of reactions the "sum" of which leads to the formation reaction; the first step being the dissolution reaction. A number of sequences are possible, but one has to select the reactions for which well-known reactants are involved. So, for a halide apatite, $\text{M}_{10}(\text{PO}_4)_6\text{X}_2$ ($\text{X}=\text{F}$ or Cl), the following succession could be proposed:



Steps 1, 3, 5, 7, and 9 correspond to dissolution of solids or dilution of concentrated acid solutions. The corresponding enthalpies are determined in the same device using the same quantities of solvent. Steps 2, 4, 6, 8 and 10 correspond to reactions of formation of well-known products or entities. Their corresponding enthalpies are picked from literature⁵.

For an hydroxyapatite $\text{M}_{10}(\text{PO}_4)_6(\text{OH})_2$ another sequence should be proposed. It contains steps 2, 3, 4, 5 and 6, but steps 7 and 8 are deleted and steps 1, 9 and 10 are replaced respectively by the following ones:



One can check that the “summation” of these combined reactions leads to the formation reaction of M-hydroxyapatite, $\Delta_f H^\circ(T_0)$.

Table 1 gathers $\Delta_f H^\circ(T_0)$ for fluor, hydroxy and chlor-apatites of Ca, Ba, Sr, Cd and Pb.

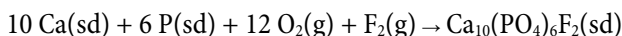
Table 1: Standard enthalpy of formation of the apatites at 25°C in kJ mol⁻¹

	Y = F	Y = OH	Y = Cl
Ca ₁₀ (PO ₄) ₆ Y ₂ [ref]	-13548[6]	-13305[6]	-13179[6]
Ba ₁₀ (PO ₄) ₆ Y ₂ [ref]	-13564[7]	-13309[7]	-13246[8]
Sr ₁₀ (PO ₄) ₆ Y ₂ [ref]	-13604[9]	-13373[9]	-13233[10]
Cd ₁₀ (PO ₄) ₆ Y ₂ [ref]	-8795[11]	-8648[9]	-8463[12]
Pb ₁₀ (PO ₄) ₆ Y ₂ [ref]	-8529[13]	-8261[14]	-8204[15]

Neglecting the entropy factor, the stabilities of these compounds can be compared on the basis of $\Delta_f H^\circ(T_0)$. Table 1 shows that fluorapatite is more stable than the corresponding hydroxyapatite, which is itself more stable than the chlorapatite. On the other hand the alkali-earth apatites form the more stable group in which $\Delta_f H^\circ(T_0)$ varies within a 3% interval. In this group, some values are very close, and so stabilities of the corresponding products couldn't be compared on the basis of the enthalpy values. The entropy term should be taken into consideration.

DETERMINATION PROCEDURE OF GIBBS ENERGY OF FORMATION

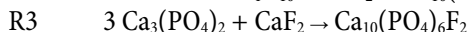
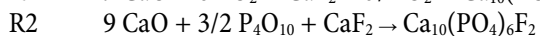
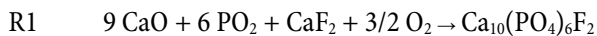
In the previous way of doing the entropy of formation is taken to equal its uppermost value, i.e. zero. However one can calculate a lower limit by combining $\Delta_f H^\circ(T_0)$ of the apatite and the standard entropy of a reaction in which the apatite is involved with other products whose entropies are tabulated. Assuming $\Delta_f S^\circ(T_0)$ of the apatite to equal this new limit leads to the standard Gibbs energy of formation, on the basis of which stabilities are discussed again. Let us take an example: for Ca/F-apatite, the formation reaction, which is written as:



is expressed as a difference between the entropy of Ca/F-apatite and those of the reactants. Taking into account the standard values of the latter ones¹⁶, $\Delta_f S^\circ(T_0)$ becomes:

$$\Delta_f S^\circ(T_0) = S^\circ(\text{Ca/F-ap}) - 2231,8 \text{ J mol}^{-1} \text{ K}^{-1} \quad (1)$$

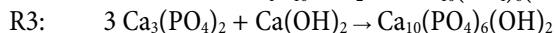
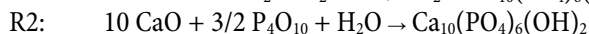
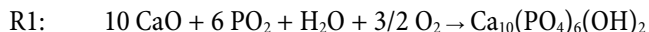
However the limit of $S^\circ(\text{Ca/F-ap})$ can be determined by involving the apatite in a reaction for which the entropies of the reactants are tabulated. Several reactions are possible; each of them leading to a limit for $S^\circ(\text{Ca/F-ap})$. The phosphorus reactants which are “entropically” known in literature are PO₂, P₄O₁₀ and Ca₃(PO₄)₂. Combining these products with other reactants, one can imagine the following reactions:



For reaction R1, $\Delta_f S^\circ = S^\circ(\text{Ca/F-ap}) - 3327,8 \text{ J mol}^{-1} \text{ K}^{-1}$. This quantity should be negative, and so taking into account relation (1), the new limit for the entropy of formation of Ca/F-apatite is: $\Delta_f S^\circ(T_0) < -1096 \text{ J mol}^{-1} \text{ K}^{-1}$. When $\Delta_f S^\circ(T_0)$ equals this limit, the standard Gibbs energy of formation of Ca/F-apatite becomes $\Delta_f G^\circ(T_0) = -13221 \text{ kJ mol}^{-1}$, which is 2,5% higher than the previous value calculated assuming $\Delta_f S^\circ(T_0)$ to equal zero ($\Delta_f G^\circ(T_0) = \Delta_f H^\circ(T_0) = -13548 \text{ kJ mol}^{-1}$).

The calculation procedure has been carried out by considering reactions R2 and R3, and the limits for $\Delta_f S^\circ(T_0)$ are -2573 and $-2551,3 \text{ J mol}^{-1} \text{ K}^{-1}$. Considering $\Delta_f S^\circ(T_0)$ as equal these limits leads for $\Delta_f G^\circ(T_0)$ to -12781 and $-12787 \text{ kJ mol}^{-1}$ respectively. These values are close each to the other and 1,5% higher than the NBS value ($-12983 \text{ kJ mol}^{-1}$, ref¹⁷). The difference comes from the ΔH value and not from ΔS . Taking for $S^\circ(\text{Ca/F-ap})$ the NBS value ($775,7 \text{ J mol}^{-1} \text{ K}^{-1}$) and replacing for $\Delta_f H^\circ(T_0)$ the NBS value (-13744) by that of table 1 ($-13548 \text{ kJ mol}^{-1}$) leads to $\Delta_f G^\circ(T_0) = -12787 \text{ kJ mol}^{-1}$.

Ca-hydroxyapatite provides another example. For this compound, $f_s S^\circ(T_0)$ can be expressed as: $\Delta_f S^\circ(T_0) = S^\circ(\text{Ca/H-ap}) - 3460,9 \text{ J mol}^{-1} \text{ K}^{-1}$. Ca/H-apatite can be involved in the three following reactions:



Assuming the entropies of these reactions to be negative leads for the entropy of formation to different limits. Taking this quantity to equal its limits, one can calculate three values for $\Delta_f G^\circ(T_0)$ of Ca/H-apatite. These values are respectively: -12950 ; -12510 and $-12509 \text{ kJ mol}^{-1}$. The NBS value is $\Delta_f G^\circ(T_0) = -12677 \text{ kJ mol}^{-1}$. It is 1,8 % lower than the two latter ones. As previously, the discrepancy (233 kJ mol^{-1}) mainly comes from ΔH value, since the difference between the ΔH -NBS value (-13477) and that of table 1 (-13305) is 172 kJ mol^{-1} .

COMPARISON OF THE APATITES STABILITIES

The previous calculation allows to conclude that the standard entropy can be correctly estimated by considering a reaction leading to the product from reactants one of them is P_4O_{10} or $\text{Ca}_3(\text{PO}_4)_2$. However reactions involving the latter can be written only for calcium apatites and not for the others. Consequently calculation of $\Delta_f S^\circ(T_0)$ for all of the products has been carried out taking into account reaction schemes in which P_4O_{10} is involved. The results, combined to the thermochemical data (table 1) lead to $\Delta_f G^\circ(T_0)$ listed in table 2. It should be emphasized that the general conclusions which have been drawn from table 1 about the relative stability of the groups, remain valid. The entropy term is not too high and so comparison of the stability between the groups can be carried out according to the enthalpy of formation. However within the alkali-earth group, the enthalpies of formation are close each to the other and the entropy term can reverse the relative stability of the compounds. That is what happens with the couple Ca/H-ap, Ba/Cl-ap. The first one is more stable than the second in the ΔH -scale, whereas it is less stable in the ΔG -scale. This is shown better in figure 1 which gathers $\Delta_f H^\circ(T_0)$ and $\Delta_f G^\circ(T_0)$ values for all the alkali-earth apatites.

TABLE 2: Standard Gibbs energy of formation at 25°C of the apatites / kJ mol^{-1}

	Y = F	Y = OH	Y = Cl
$\text{Ca}_{10}(\text{PO}_4)_6\text{Y}_2$	-12781	-12510	-12418
$\text{Ba}_{10}(\text{PO}_4)_6\text{Y}_2$	-12834	-12553	-12519
$\text{Sr}_{10}(\text{PO}_4)_6\text{Y}_2$	-12845	-12587	-12478
$\text{Cd}_{10}(\text{PO}_4)_6\text{Y}_2$	- 8045	- 7873	- 7719
$\text{Pb}_{10}(\text{PO}_4)_6\text{Y}_2$	- 7782	- 7482	- 7458

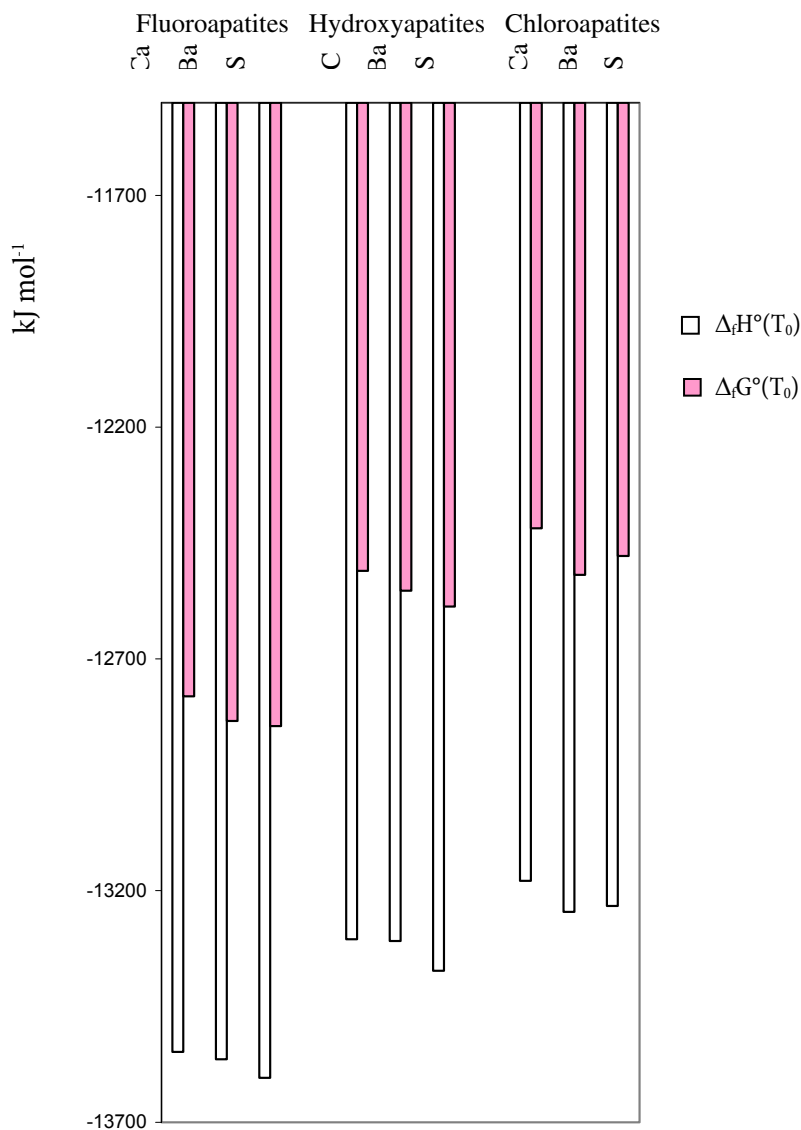


Figure 1: $\Delta_f H^\circ(T_0)$ and $\Delta_f G^\circ(T_0)$ for alkali-earth apatites/ kJ mol^{-1}

CONCLUDING REMARK

Calculation of the Gibbs energy of formation leads to a more realistic stability scale when the enthalpy terms are close each of the other. This is particularly true for alkali-earth apatites.

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