CORPUS PUBLISHERS

Journal of Mineral and Material Science (JMMS)

Volume 3 Issue 4, 2022

Article Information

Received date :September 06, 2022

Published date: October 14, 2022

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Opinion

Solution Enthalpy of Calcium Oxyapatite $Ca_{10}(PO_4)_6O$ in Pure Water

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Opinion

Questions related to the relative stability, solubility, precipitation of apatites in aqueous media are regularly arised [1,2] for two foremost reasons. The first reason is that apatites are involved in numerous fields, counting medical and biomaterials sciences (bone tissue engineering, nanomedicine [3], anthropology [4], geology/mineralogy [5], or else other environmental sciences (immobilization of phosphates and metallic compounds, nuclear sciences [6,7], where handling these materials needs knowledge of their stability and other dissolution properties in water. The second one is that, for fundamental purposes, the need for reliable and readily usable thermodynamic data in terms of Gibbs free energies, enthalpies, entropies, or else heat capacities is evident. So far, there is only a rare literature addressing the thermodynamic properties of apatites [1]. Moreover, calcium oxyapatite has an interest in the field of biomaterials and dental implants [8] and is used for medicine carrier [9]. Nevertheless, its solution enthalpy in pure water is not known. In fact, it can be deduced from the results previously found in studies on calcium hydroxyapatite CaHap [10,11]. The reaction of the formation of CaHap by hydration of CaOap can be written as eq.1:

$$Ca_{10}(PO_4)_6O(CaOap) + H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2(CaHap) \quad (1)$$

whose enthalpy is first written from the standard enthalpies of formation:

$$\Delta_r H° = \Delta_f H°(CaHap) - \Delta_f H°(H_2O) - \Delta_f H°(CaOap)$$

From data displayed in Table 1, $\Delta_r H°$ can be determine, the value found is -102.2 kJ mol^{-1}, with

$$\Delta_f H°(H_2O_{liq}) = -285.8 \text{ kJ mol}^{-1} \ [12]$$

Similarly, $\Delta_r H°$ can be deduced from the enthalpies of some hypothetical dissolutions of the various terms of the reaction in pure water as:

$$\Delta_r H° = \Delta_{sol} H°(CaOap) + \Delta_{sol} H°(H_2O) - \Delta_{sol} H°(CaHap).$$

Finally, the solution enthalpy of CaOap in pure water can be deduced combining the two equalities:

$$\Delta_{sol} H°(Oap) = -495.8 \text{ kJ mol}^{-1}.$$

Then, the advantage of all this research on the determination of the solution enthalpy of apatites in water, by the dissolution model as stated in previous works [10,13], is to furnish thermodynamic data on the solution of calcium apatites, as shown in Table 1. When it comes to the stability of calcium apatites, the free energy of formation $\Delta_f G°$ of some apatites, is also displayed in Table 1. We notice that the more the apatite is stable, the more the respective solution energy in pure water is small, while being exothermic in all cases. This fact, states that the calcium apatites have a retrograde dissolution in water with the temperature, taking into account the Vant'Hoff low at constant atmospheric pressure [14].

Table 1: Standard enthalpies of formation, of solution in water and the free energy of formation of the studied apatites. *present work.

	$\Delta_f H°$ (298K) kJ mol^{-1}	$\Delta_f G°$ (298K) kJ mol^{-1}	$\Delta_{sol} H°$ (298K) at pH=7 kJ mol^{-1}
<CaFap>	-13548 [17]	-12826 [19]	-275.1 [14]
<CaHap>	-13305 [11]	-12510 [20]	-393.6 [18]
<CaOap>	-12917 [6]	-12272 [19]	-495.8*

Moreover, oxyapatites are considered as potential drug carriers for the delivery of a variety of pharmaceutical molecules since such calcium apatites can be mesoporous [15,16]. That's why investigating intrinsic physico-chemical parameters, and studying the thermodynamics of these compounds, such as solution enthalpies, could shed light on the mechanisms controlling the activity of these important and promising medical apatite-based-materials [17-20].

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