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Effect of temperature on the attack of fluorapatite by a phosphoric acid solution

Khamaïs Brahim, Kaïs Antar, Ismaïl Khattech* and Mohamed Jemal

Faculty of Science, Chemistry Department, Applied Thermodynamics Laboratory, 2092 Tunis El Manar – Tunisia.

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The attack of fluorapatite (Fap) by phosphoric acid solution between 25 and 65 °C was followed by microcalorimetry. The molar enthalpy decreases until a temperature close to 45 °C, and then increases. This behaviour was attributed to a change of mechanism. Iteration of the results enables us to propose a two or one step mechanism, depending on the temperature range. Kinetic and thermochemical parameters corresponding to each step were also deduced. For temperature lower than 45 °C, the activation energy, E_a , equals about 20 kJ mol⁻¹, suggesting a diffusion phenomenon control, whereas for higher temperature the attack seems to be controlled by a chemical process ($E_a = 101$ kJ mol⁻¹).

Key words: Kinetics, microcalorimetry, fluorapatite, phosphoric acid, temperature, dissolution.

INTRODUCTION

The main factors affecting the reaction rate of acid attack of phosphates are: acid concentration, solid/liquid ratio, particular size and temperature (Huffmann et al., 1957; Meikhov and Dorozhkin, 1990; Gioia et al., 1977; Grinevich et al., 1983; Shakourzadeh et al., 1984; Sluis et al., 1987a, b; Dorozohkin and Prakt, 1996; Sevim et al., 2003; Elmore and Farr, 1940; Bayramoglu et al., 1995; Samir et al., 2001; Sikdar et al., 1978; Abali et al., 1997; Yarstri et al., 1994). In previous works (Brahim et al., 2005; Brahim et al., 2006), we have studied the solid/liquid ratio and the concentration effects on both the kinetics and nature of the products formed during the attack of a synthetic fluorapatite, Ca₁₀(PO₄)₆F₂, by phosphoric acid solutions. We showed that, for 10, 18, and 30% weight P₂O₅ solutions and a low solid/liquid ratio, the kinetic results can be interpreted by a mechanism comprising a physical diffusion, phenomenon followed by a chemical process which we attributed to the complex formation, Ca(H₂PO₄)⁺ (Brahim et al., 2005). Increasing the solid/liquid ratio led to the formation of monohydrate monocalcic phosphate (Ca(H_2PO_4)₂, H_2O) or to a mixture of the latter solid and dehydrate bicalcic phosphate

(CaHPO₄, 2H₂O) (Brahim et al., 2006).

The aim of the present work was to study the temperature effect on the phosphoric acid attack of a synthetic fluorapatite. Many authors have studied this effect on the kinetics of this reaction (Sevim et al., 2003; Elmore and Farr, 1940; Bayramoglu et al., 1995; Abali et al., 1997; Yarstri et al., 1994; Ben Brahim et al., 1999). Most of them have focused on the attack of natural phosphate ores and the conclusions are somewhat contradictory. For instance some studies performed on the attack a Turkish phosphate ore by HCI/HOCI solution (Abali et al., 1997) or sulfuric acid solution (Yarstri et al., 1994), showed that over 40℃, the reaction rate decreases with increasing temperature. An other work performed on a Tunisian phosphate ore (from Gafsa), in the temperature range 25 - 60℃, have showed that increasing temperature led to the decrease of the attack rate (Ben et al., 1999). On the other hand, the attack of a phosphate ore by a phosphoric acid solution, performed by Sluis et al. (1987a) in the temperature range 60 - 90°C, has led to an increase of the rate when increasing temperature. A similar conclusion has been obtained by other authors with nitric or sulfuric acid solution (Sevim et al., 2003; Bayramoglu et al., 1995). The fluorapatite (or Fap) used in this work was prepared by the double decomposition method recommended by Heughebaert et al. (1977). The attack reaction was followed using a C-80 SETARAM Calori-

^{*}Corresponding author. E-mail: khattech@fst.rnu.tn. Tel: +21698208884; Fax: +216 71885 008.

Temperature (℃)	ΔH _{mes} (kJmol ⁻¹)	Δ₁H (kJmol ⁻¹)	Δ₂H (kJmol ⁻¹)	$(\Delta_1 H + \Delta_2 H) = \Delta H_{cal}$ (kJ mol ⁻¹)	k ₁ . 10 ³ (s ⁻¹)	k ₂ (mol L ⁻¹ s ⁻¹)
25	- 171.0	- 181.1	10.3	- 170.8	8.33	1783
30	- 183.1	- 190.5	10.0	- 180.5	9.67	1782
35	- 190.6	- 196.2	9.8	- 186.4	10.91	1783
40	- 194.9	- 202.3	10.2	- 192.1	12.23	1783

Table 1. Enthalpy deduced by integrating the rough signal (ΔH_{mes}) and kinetic and thermodynamic parameters deduced iteratively from relation (1).



Figure 1. Measured enthalpy as a function of temperature.

meter. The reversal cells of the latter have been previously provided with electrical resistances in order to perform calibration operations in the reacting cell, and so the time constants were determined in the same conditions that the chemical process. The recorded signals were processed according the procedure developed in previous papers (Brahim et al., 2005; Brahim et al., 2006), to give the deconvoluted curves.

EXPERIMENTAL RESULTS

Experiments were performed with a few amount of solid compared to the solution and the solid/liquid ratio has been maintained practically the same by dissolving masses of Fap very close to 30 mg in 4.5 mL of phos-phoric acid solution having 18% weight P_2O_5 . The resulting measured enthalpy, ΔH_{mes} , determined by integrating the rough signal is represented as a function of temperature in the range of 25 - 65 °C (Figure 1). For higher temperatures, large fluctuations of the base line were observed, resulting probably from a poor tightness between the two compartments of the reacting cell. Figure 1 shows an extremum at about 45 °C which can be attributed to a modification in the attack mechanism. This assumption is confirmed below.

Interpretation of the results

For temperature lower than 45 °C

In a previous work, undertaken at $25 \,^{\circ}$ C (Brahim et al., 2005), we have showed that the kinetic results could be interpreted by a two successive step process which can be represented by the following scheme:

$$A + sol \xrightarrow{(1)} B \xrightarrow{(2)} C$$

with k_1 , k_2 , $\Delta_1 H$ and $\Delta_2 H$ are the rate constants and the molar enthalpies of step (1) and (2) respectively. These parameters were deduced iteratively by searching the better agreement between the deconvoluted thermogram and the calculated curve. The latter is given by the following expression:

$$\frac{dq}{dt} = \frac{m_A}{M_A} \left[\frac{\Delta_2 H \ k_1 k_2}{k_1 - k_2} (exp(-k_2 t) - exp(-k_1 t)) + \Delta_1 H \ k_1 exp(-k_1 t) \right]$$
(1)

with M_A , the molar mass of Fap and m_A its mass initially introduced.

This expression has been tried to the results obtained for higher temperature, but the agreement between thermogenesesis and calculated curves was obtained only for temperatures lower than 45°C. Table 1 gathers kinetic and thermodynamic parameters deduced iteratively using expression (1), and the enthalpies deduced by integrating the rough signal (ΔH_{mes}) for temperature up to 40 °C. We can notice that the values of latter quantity don't differ from the sum (Δ_1 H + Δ_2 H) by more than 2.2%. So we can suggest that, for a temperature range 25 to 40℃, the attack process is the same as proposed previously (Brahim et al., 2005), and includes a two successive step process which can be attributed to the following reactions: $Ca_{10}(PO_4)_6F_{2 (s)} + 14 \{H_3PO_4\}_{sol} \rightarrow \{10 Ca^{2+} + 20 H_2PO_4\}$ + 2 HF}_{sol} (I) 10 {Ca²⁺}_{sol} + 10 {H₂PO₄}_{sol} \rightarrow 10{Ca(H₂PO4)⁺}_{sol} (II)

Table 1 shows that the rate constant k_2 is not affected by temperature, suggesting a very small activation energy for reaction (II). However the plot of $ln(k_1)$ as a function of $\frac{1}{T}$ (Figure 2) is represented by a straight line leading



Figure 2. Plot of $ln(k_1) = f(1/T)$ for temperature lower than $45^{\circ}C$.

to an activation energy of 19.8 kJ mol⁻¹ for reaction (1). This value is in the same order of magnitude that ones deter-mined by many authors, which are in the range of 15 to 29 kJ mol⁻¹ (Huffmann et al., 1957; Sluis et al., 1987a; Sevim et al., 2003; Yarstri et al., 1994; Ben et al., 1999).

For temperature higher than 45°C

Kinetic law: Application of expression (1) to the results obtained in the temperature range 45 to 65°C led to a very large discrepancy between deconvoluted and calculated curves. Moreover the enthalpies deduced iteratively were far from the measured ones. However, the assumption of a one step mechanism led to more realistic results. In our experimental conditions, the phosphoric acid quantity is too large compared to the solid amount, assuming the disappearance rate of the latter increases as the difference between the final and instantaneous concentrations increases, the dissolution rate of the solid, r, can be expressed as :

$$r = -A \frac{dm_t}{dt} = k(C_o - C)^n$$
⁽²⁾

with m_t: mass of solid Fap at time t, k: apparent rate constant, A: adjustment factor for unities, C_o: Fap concentration at the end of dissolution, C: concentration of dissolved Fap at time t, n: partial order with respect to Fap. The Fap mole number dissolved at time t, nt, is the

difference between the initial mole number (i) and the reacting one (reac). So expression (2) can be written as follows:

$$r = -A \frac{dm_t}{dt} = k (\frac{m_i - m_{reac}}{MV})^n = k (\frac{m_i}{MV})^n (1 - X)^n$$
(3)

with
$$X = \frac{m_{réac}}{m_i}$$
 (conversion rate)

M is the molar mass of Fap and V is the volume of the liquid. So

$$\frac{dm_t}{dt} = -\frac{k}{A} \left(\frac{m_i}{MV}\right)^n (1 - X)^n \tag{4}$$

m_{reac} and m_i can be expressed respectively as a functions of the heat quantities (q) released at time t and (Q) resulting from the whole of the reaction, by the following expressions:

$$m_{\text{reac}} = \frac{q}{\Delta H} M \tag{5}$$

$$m_i = \frac{Q}{\Delta H} M \tag{6}$$

With Δ_r H: molar enthalpy of reaction.

dq These expressions enable to express the heat flow dt

as follows:

$$\frac{dq}{dt} = -k \frac{\Delta H}{MA} \left(\frac{m_i}{MV}\right)^n \left(1 - \frac{q}{Q}\right)^n \tag{7}$$

agreement between calculated and deconvoluted curves. Figure 3 shows an example of iteration result for T =60°C. We can notice a good coincidence between the theoretical (Figure 3a) and deconvoluted (Figure 3b) curves. Moreover, the enthalpies deduced iteratively, ΔH_{it} , are very close to the values deduced by integrating the rough signal (ΔH_{mes}) (Table 2). This table summarizes also values of the partial order n and the apparent rate constant. The average of n is close to 1, this order value has been adopted previously by many authors for the acid attack of synthetic or natural phosphates (Huffmann et al., 1957; Sluis et al., 1987a; Sevim et al., 2003; Iteration of equation (7) was undertaken by searching values of k, $\Delta_r H$ and n parameters leading to the better Bayramoglu et al., 1995; Yarstri et al., 1994; Ben et al., 1999).

The plot of ln(k) as a function of 1/T is represented by a straight line (Figure 4) leading to an activation energy E_a = 101.1 kJ mol⁻¹. This value is close to the one determined by Bayramogu et al. (1995) (99.5 kJ mol⁻¹) for the attack of a phosphate ore by nitric acid. These authors attributed this value to the H⁺ ions diffusion from the solution to the solid surface.

Reactional scheme: For temperature higher than 45°C, the global enthalpy of the attack is lower than the one corresponding to the simple dissolution of the solid, $\Delta_1 H$ (Table 1). It could be suggested that the difference result

i	iteratively or from integration of the rough peak.							
	Temperature (℃)	50	55	60	65			

Table 2. Rate constant, partial order and molar enthalpy of the reaction, deduced

Temperature (℃)	50	55	60	65
- ΔH _{mes} (kJ mol ⁻¹)	200.4	198.1	189.4	184.6
- ΔH _{it} (kJ mol⁻¹)	202.4	197.8	190.2	185.7
Partial order : n	1.15	0.98	1.05	1.08
Rate constant k.10 ³ (s ⁻¹)	11.2	15.3	29.2	55.7



Figure 3. Iteration result of the Equation (7) (a) and thermogenesis (b) determined for dissolution of 30.01 mg Fap in 4.5 mL of H_3PO_4 solution.



Figure 4. Plot of ln(k) = f(1/T) for temperature higher than $45^{\circ}C$.

results from the variation the enthalpy of reaction (1) with temperature, according to Kirchhoff law. Suppose the heat capacity of reaction (1), $\Delta_1 C_p$, is constant, the Kirchhoff relation will be expressed as follows:

$$\Delta_{1}H(T) = \Delta_{1}H^{o}(T_{o}) + \Delta_{1}C_{p}(T-T_{o})$$
(8)

with
$$T_o = 25 \,^{\circ}{\rm C}$$



Figure 5. Variation of $\Delta_1 H$ enthalpy as function of $(T-T^\circ)$ for temperature lower than 45 °C.

Figure 5 shows the plot of $-\Delta_1$ H, obtained for temperature lower than 45 °C (Table 1) as a function of $(T-T_o)$. The slope of the curve enables to calculate the heat capacity of reaction (1), $\Delta_1 C_p = -1.38$ kJ K⁻¹ mol⁻¹. For temperature higher than 45 °C, calculation of Δ_1 H according to expression (8) led to values lower than ones deduced by-iteration (Table 3). It could be suggested that the difference results from an endothermic reaction following the dissolution of the solid. Taking into account the results obtained in a previous work (Antar and Jemal, 2006), neutralisation of H₂PO₄⁻ by H⁺ has been considered as a complementary reaction.

Neutralisation enthalpy of H₂PO₄

Enthalpy of $H_2PO_4^-$ neutralisation by H^+ was measured at different temperature in conditions similar to that corresponding to the attack by phosphoric acid (18% P_2O_5). To do so, a mass of solid (NaH₂PO₄.2H₂O) was dissolved in phosphoric acid solution (18% P_2O_5) so that the concentration of $H_2PO_4^-$ in the final solution is in the same order of magnitude of that obtained by dissolving 30 mg of Fap. A series of experiments were performed by mixing similar masses of the previous solution with 4.5 mL of phosphoric acid solution (18% P_2O_5). Figure 6 shows the plot of neutralisation molar enthalpy, $\Delta_{neut}H(T)$, as a function

Table 3. (Comparison o	of enthalpies	deduced by	different wa	ys (see text).
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Temperature (°C)	50	55	60	65
$\Delta_{1}H(T) = \Delta_{1}H^{o}(T_{o}) + \Delta_{1}C_{p}(T-T_{o}) (kJ mol^{-1})$	-216.6	-223.5	-230.4	-237.3
$\Delta H_{it} (kJ mol^{-1})$	-202.4	-197.8	-190.2	-185.7
ΔH _{mes} (kJ mol ⁻¹)	-200.4	-198.1	-189.4	-184.6
$\Delta H_{cal} = (\Delta_1 H+ 20 \Delta_{neut} H) \text{ kJ mol}^{-1} \text{ (by Fap mol)}$	-200.3	-199.6	-196.4	-197.7



Figure 6. Enthalpy of neutralization as a function of temperature

of temperature in the range of $30 - 65 \,^{\circ}$ C. We can notice the endothermic effect of neutralisation reaction which begins to shift at about $45 \,^{\circ}$ C.

Reactional mechanism

In the assumption of a mechanism comprising a solid dissolution [reaction (1)] followed by the neutralisation of 20 moles of $H_2PO_4^-$ ions, the global enthalpy will be calculated as follows:

$$\Delta H_{cal} = \Delta_1 H + 20 \Delta_{neut} H \tag{9}$$

and its values are reported in Table 3. We can notice that values of ΔH_{cal} are close to the ones determined iteratively, ΔH_{it} . Thus it could be suggested that, for temperature higher than 45 °C, the mechanism comprises the dissolution of the solid into Ca²⁺ and H₂PO₄⁻ followed by the neutralisation of the anion, the second step being much faster than the first, and the global reaction could be as follow:

As a concluding remark, some papers dealing with phosphate ore attack agree with a diminution of the reaction rate near 40° C when increasing temperature. Our results show rather a mechanism change at a temperature around 45 °C. Moreover the low value of activation energy below 45 °C suggests a diffusion phenomenon, while for higher temperature the attack reaction seems to be controlled by a chemical process.

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