

Kinetics and thermodynamics of the attack of fluorapatite by a mixture of sulfuric and phosphoric acids at 55 °C

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Abstract

A calorimetric study of kinetics and thermodynamics of the attack of a synthetic fluorapatite by a mixture of sulfuric and phosphoric acids is undertaken at 55 °C. The global enthalpy of the attack equals -409.3 kJ/mol. The recorded thermograms show two peaks leading to calcium sulfate hemihydrate and dihydrate, respectively. The deconvoluted curves were analysed iteratively. A kinetic mechanism based on simultaneous reactions has been proposed for the first peak and confirmed thermochemically by comparing the enthalpies deduced from iteration and that determined from experimental and calculated routes. The second peak of the thermogram was attributed to transformation of calcium sulfate hemihydrate into gypsum according to a dissolution/precipitation scheme. These phenomena are of order one and two, respectively.

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1. Introduction

In a previous work [1] we have carried out a kinetic and thermodynamic study of the attack of a synthetic fluorapatite (Fap) by a solution of sulfuric and phosphoric acids at 25 °C using a C-80 SETARAM calorimeter. Acid solution was prepared by mixing 80% volume of a phosphoric acid solution having 20% weight P_2O_5 , with 20% volume of sulfuric acid (90% weight H_2SO_4). The attack resulted in one peak on the rough and deconvoluted signals. Interpretation of the results by Avrami model showed the existence of two steps. The first one has been attributed to the dissolution of the solid, and the second to precipitation of gypsum. The deconvoluted curves were also analysed iteratively to obtain the kinetic parameters and the enthalpy of precipitation. This latter quantity is close to that determined calorimetrically in complementary experiments.

These experiments have been carried out at higher temperature (with 5° intervals) and the results showed the appearance of a new phenomenon which resulted in a new peak on the thermogram following the one corresponding to dissolution of Fap. That peak departs progressively from the first one as the temper-

ature increases; and both are completely separated at 55 °C, then the second one becomes very faint in intensity and widespread over time. The aim of the present work was to propose an attack mechanism through the analysis of calorimetric measurements obtained at 55 °C using the same acid mixture. As in the preceding work, experiments were carried out on fluorapatite (or Fap) prepared by the double decomposition method recommended by Heughebaert [2] and the recorded signals were processed according the procedure developed in previous papers [1,3] in order to get the deconvoluted curves.

2. Thermodynamic study

After the stabilisation time at 55 °C, experiments were carried out by dissolving m (mg) of Fap in 4.5 mL of acid mixture. The deconvoluted thermograms show two peaks having a large difference in intensity. Fig. 1 gives an example of the rough and the deconvoluted thermograms corresponding to the first peak for 39.41 mg of Fap. Because of the rapidity of the phenomenon related to that peak, there is a large discrepancy between the rough and deconvoluted signals. However for the second peak, the signals coincide. Fig. 2 shows a perfect superposition of them followed by a faint difference at the end of the peak, indicating a very slow corresponding phenomenon.

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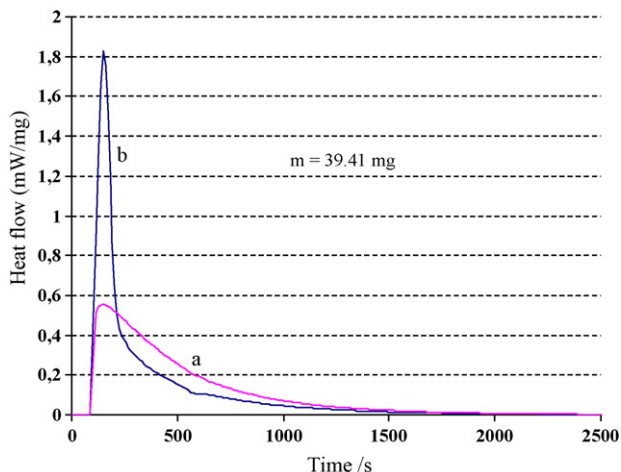


Fig. 1. Thermogram (a) and thermogenesis (b) corresponding to the first peak.

The enthalpy measured by integrating the global rough signal is represented as a function of dissolved Fap mass by a straight line of equation $y = 0.40767m + 0.4095$, with y in J and m in mg. The slope of the curve enables to calculate a global enthalpy: $\Delta H = -409.3 \pm 2.1 \text{ kJ mol}^{-1}$. This value is close to the enthalpy determined at 25°C in the previous work ($-407.0 \pm 1.7 \text{ kJ mol}^{-1}$) [1]. IR spectroscopy and X-ray diffraction show that gypsum was obtained at the end of the attack. However the solid isolated after the first peak shows absorption bands similar to that recorded by Mandal and Mandal [4] for calcium sulfate hemihydrate, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$. So the second peak corresponds to the transformation of calcium hemihydrate into gypsum.

The drawing of the enthalpies determined by integrating the first and the second rough peaks as a function of Fap mass led to equations $y = 0.2767m - 0.0884$ and $y = 0.1299m + 0.4979$, respectively. The enthalpies resulting from the slopes equal -278.7 ± 2.1 and $-130.6 \pm 2.1 \text{ kJ mol}^{-1}$ Fap. That corresponds to -27.9 and $-13.1 \text{ kJ mol}^{-1}$ of appearing calcium sulfate hemihydrate and dihydrate, respectively. The latter value is a bit higher than that determined by combining the formation

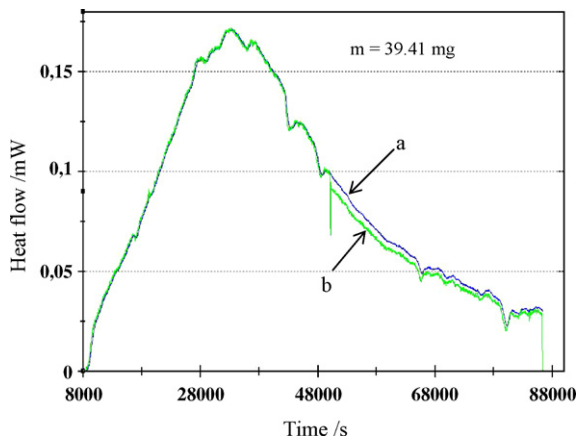


Fig. 2. An example of thermogram (a) and thermogenesis (b) corresponding to the second peak.

enthalpies of calcium hemihydrate [5], calcium dihydrate and water [6] ($-17.18 \text{ kJ mol}^{-1}$).

3. Kinetic mechanism for the first peak

3.1. Kinetic law

Determination of the transfer function parameters allowed to calculate the deconvoluted curve for each dissolved Fap mass. In order to access to the attack mechanism corresponding to the first peak, a number of hypothesis have been made and the resulting heat flow has been derived. However the only mechanism leading to a better coincidence between the calculated heat flow and the deconvoluted curves consists of a two successive step process. In this process a reagent A (Fap) is dissolved in the solution to give a B product which transforms into C according to the following scheme:



Suppose these reactions are of order 1 with regard to A and B, respectively, the equation rates are in the form:

$$r_1 = k_1 c(A) \quad (1)$$

$$r_2 = k_2 c(B) \quad (2)$$

where $c(A)$ and $c(B)$ are the concentrations of A and B, respectively.

The first reaction is not disturbed by the second so the concentration of reagent A is given by the relation below:

$$c(A) = c_0(A) \exp(-k_1 t) \quad (3)$$

with $c_0(A)$ is the initial concentration of A.

On the other hand, the component B formed by the initial reaction is consumed by the second.

Its global appearance rate would be expressed as:

$$r(B) = r_1 - r_2 \quad (4)$$

thus:

$$\frac{-dc(B)}{dt} = k_2 c(B) - k_1 c(A) \quad (5)$$

Integrating this equation leads to the following expression for the concentration of B:

$$c(B) = c_0(A) \frac{k_1}{k_1 - k_2} [\exp(-k_2 t) - \exp(-k_1 t)] \quad (6)$$

Conservation of the mass implies that at any moment the sum of the concentrations of species A, B and C equal the initial concentration of reagent A, and so:

$$c(A) + c(B) + c(C) = c_0(A)$$

thus:

$$c(C) = c_0(A) \left(1 - \frac{k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)}{k_2 - k_1} \right) \quad (7)$$

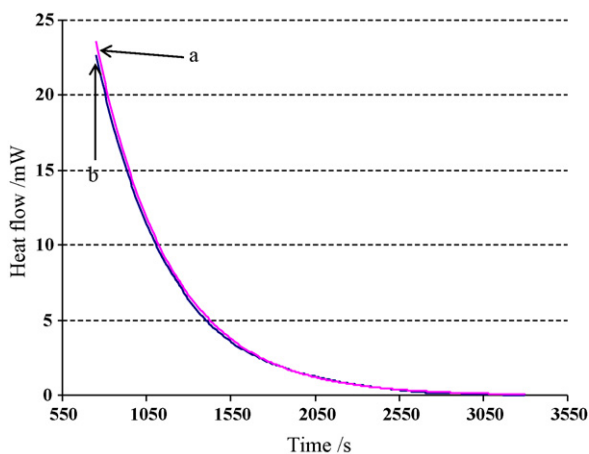


Fig. 3. Iteration result of the Eq. (10) (a) and thermogenesis (b) corresponding to $m = 86.10$ mg.

If q_1 denotes the quantity of heat released at time t for the transformation of a quantity of matter of A into B, then:

$$q_1 = [c_o(A) - c(A)]V\Delta_1H \quad (8)$$

with V : volume of the reactional medium; Δ_1H : the molar enthalpy of reaction (I).

The quantity of heat q_2 resulting from the transformation of a quantity of B into C is expressed as:

$$q_2 = c(C)V\Delta_2H \quad (9)$$

with Δ_2H : the molar enthalpy of reaction (II).

The total heat (q) measured during the experiment is the sum:

$$q = q_1 + q_2$$

In addition, expressions of $c(A)$ and $c(C)$, given, respectively, by relations (3)–(7), allow to express the heat flow dq/dt as follows:

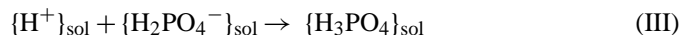
$$\frac{dq}{dt} = \frac{m_A}{M_A} \left[\frac{\Delta_2 H k_1 k_2}{k_1 - k_2} (\exp(-k_2 t) - \exp(-k_1 t)) + \Delta_1 H k_1 \exp(-k_1 t) \right] \quad (10)$$

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

Fig. 3 shows an example of the result of the iteration for $m = 86.10$ mg of dissolved Fap. We can notice a good agreement between the theoretical curve given by the Eq. (10) and the deconvoluted signal. For m in the range of [39.41; 86.10 mg], the agreement is obtained with values of k_1 , k_2 , Δ_1H and Δ_2H pertaining to the intervals: $[2.61 \times 10^{-3}; 2.71 \times 10^{-3} \text{ s}^{-1}]$, $[3.46 \times 10^{-1}; 3.86 \times 10^{-1} \text{ mol L}^{-1} \text{ s}^{-1}]$, $[-150.1; -149.9 \text{ kJ mol}^{-1}]$ and $[-120.5; -120.1 \text{ kJ mol}^{-1}]$, respectively. One can notice the slight variations of these parameters. Furthermore the sum of the enthalpies ($\Delta_1H + \Delta_2H$) does not differ from the enthalpy determined by integrating the first peak of the rough signal ($-278.7 \text{ kJ mol}^{-1}$) by more than 3%.

In a recent work [7], not yet published, performed on the reaction of only phosphoric acid on Fap at a temperature up to 65°C ,

Brahim showed that the results are in agreement with the existence of two mechanisms depending on the temperature range. The low temperature one is a two-step process, and at T higher than 45°C a one step mechanism occurs leading to the ionic entities Ca^{2+} and H_2PO_4^- with an enthalpy of $-198.0 \text{ kJ mol}^{-1}$ Fap at 55°C . This value is lower than Δ_1H determined iteratively for the first step. It could be suggested that the difference between these values results from the neutralisation reaction of H_2PO_4^- according to the scheme:



3.2. Thermochemical justification

Enthalpy of reaction (III) has been measured in conditions similar to that corresponding to the attack by the acid mixture. To do so, various masses of a $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$ solution have been added to 1.5 mL of acid mixture at 55°C and the resulting enthalpy was measured. The $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$ solution was prepared by dissolving 2.4273 g of solid $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ in 126.1363 g of a phosphoric acid solution (20% P_2O_5). These quantities have been chosen in order to get in the final solution a H_2PO_4^- concentration in the same order of magnitude of that obtained in Fap acid mixture. The measured enthalpy can be expressed by a parabolic law as: $\Delta H_{\text{I}} = 10^{-5}m^2 - 0.0278m + 1.2217$, where m is the mass of $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$ solution (Fig. 4(a)). However, ΔH_{I} corresponds not only to H_2PO_4^- neutralisation but also to dilution of H_3PO_4 in the mixture of phosphoric and sulfuric acids. The enthalpy of that dilution has been determined by mixing variable masses of phosphoric acid solution (20% P_2O_5) to acid mixture (1.5 mL), Fig. 4(b). The neutralization enthalpy can be deduced from the difference between the heat quantities given by curves (a) and (b) for a given phosphoric acid mass, and so for a given $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ mass. The plot of this difference (in joules) as a function of the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ mass (mg) in the $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$ solution, calculated in the latter solution, is represented by a straight line having 0.0178 as a slope, from which the neutralization enthalpy can be deduced as $+2.78 \text{ kJ mol}^{-1}$ H_2PO_4^- or $+55.6 \text{ kJ mol}^{-1}$ Fap. Adding this quantity to the ΔH corresponding to dissolution of Fap at 55°C ($-198.0 \text{ kJ mol}^{-1}$

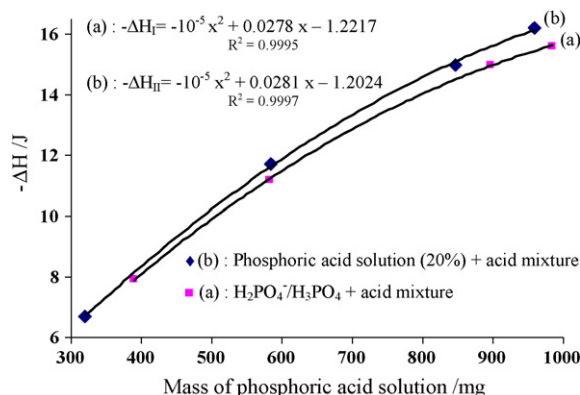
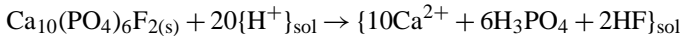
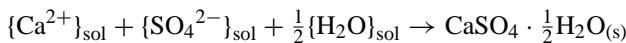


Fig. 4. Measured enthalpy versus mass of phosphoric acid solution (20%) for the two experiment series (see text).

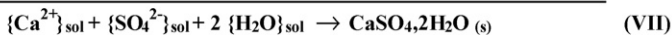
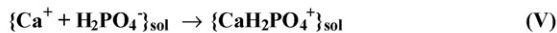
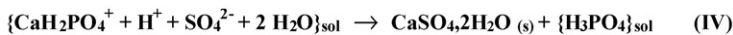
[7]) leads to $-142.4 \text{ kJ mol}^{-1}$ Fap. This value does not differ from the one deduced iteratively ($-150.0 \text{ kJ mol}^{-1}$) by more than 5.3%. Thus it could be suggested that the first step of the first peak in the deconvoluted curve corresponds to the dissolution of Fap into Ca^{2+} and H_2PO_4^- followed by the neutralisation of the anion; the second step being much faster than the first, and the global reaction could be as follows:



The second reaction in the first peak would correspond to precipitation of calcium sulfate hemihydrate according to the scheme:



With an enthalpy of $-12.03 \text{ kJ mol}^{-1}$ of hemihydrate. This value can be compared to the one calculated by combining the enthalpy of precipitation of gypsum from Ca^{2+} and SO_4^{2-} ions, and the enthalpy of transformation of hemihydrate into gypsum. The latter quantity ($-13.06 \text{ kJ mol}^{-1}$) was calculated from integration of the second peak of the thermogram obtained at 55°C . However the first one can be deduced by combining the following reactions:



Enthalpy of reaction (IV) was determined experimentally in a previous work [1] at 25°C and its value is -22.4 kJ by gypsum mole. The complex ($\text{CaH}_2\text{PO}_4^+$) formation enthalpy (reaction (V)) was determined iteratively by Brahim et al. [3] and its value is $+1 \text{ kJ}$ per complex mole. Finally the reaction (VI) enthalpy was measured above ($-2.78 \text{ kJ mol}^{-1}$) at 55°C . So the precipitation enthalpy of gypsum from the ions Ca^{2+} and SO_4^{2-} (reaction (VII)) equals -24.18 kJ per gypsum mole. Taking into account the transformation of hemihydrate into gypsum ($-13.06 \text{ kJ mol}^{-1}$) leads to $-11.12 \text{ kJ mol}^{-1}$ for the enthalpy of precipitation of hemihydrate from Ca^{2+} and SO_4^{2-} . This value is close to the mean one determined iteratively ($-12.03 \text{ kJ mol}^{-1}$), and so comparing the enthalpies deduced from iteration and that calculated by combining experimental and calculated values enables to propose chemical processes for the various steps of the mechanism.

4. Kinetics of transformation of hemihydrate into gypsum

As mentioned previously, the second peak was attributed to the hemihydrate dihydrate transformation. IR spectroscopy and X-ray diffraction confirmed this attribution.

There is a common agreement in literature according to which hydration of hemihydrate takes place through a solution route [8–11]. Hemihydrate first dissolves into ions then dihydrate, which is less soluble, precipitates from the aqueous solution. At 55°C , as the two peaks are separated, one can easily assume that precipitation of hemihydrate along the first peak occurs until

the solution reaches the saturation concentration, C_e . Suppose along the second peak, the rate of hemihydrate dissolution is proportional to the undersaturation concentration ($C_e - [\text{Ca}^{2+}]$) and that of precipitation of dihydrate is of second order with respect to calcium ions, as at 25°C [1]. The rates of these reactions can be written, respectively, as follows:

$$r_{\text{dis}} = k'_1(C_e - [\text{Ca}^{2+}])$$

$$r_{\text{pp}} = k'_2[\text{Ca}^{2+}]^2$$

where k'_1 and k'_2 are constant rate.

The global rate is controlled by the Ca^{2+} concentration, so:

$$\frac{d[\text{Ca}^{2+}]}{dt} = r_{\text{dis}} - r_{\text{pp}} \quad (11)$$

$$\frac{d[\text{Ca}^{2+}]}{dt} = k'_1(C_e - [\text{Ca}^{2+}]) - k'_2[\text{Ca}^{2+}]^2$$

so

$$\frac{d[\text{Ca}^{2+}]}{dt} + k'_2[\text{Ca}^{2+}]^2 + k'_1[\text{Ca}^{2+}] = k'_1 C_e \quad (12)$$

Usual methods for resolution did not make it possible to solve this equation. But Maple 6 software gave the two following solutions:

$$[\text{Ca}^{2+}] = \frac{1}{2k'_2} \left[-k'_1 + C_1 \text{th} \left(\frac{C_1}{2} t + \ln(C_2) \right) \right] \quad (13)$$

and

$$[\text{Ca}^{2+}] = \frac{1}{2k'_2} \left[-k'_1 + C_1 \text{th} \left(\frac{C_1}{2} t + \ln(-C_2) \right) \right] \quad (14)$$

With C_1 and C_2 two constants depending both on k'_1 , k'_2 and C_e .

$$C_1 = \sqrt{4k'_1 C_e k'_2 + k'^2_1}$$

and

$$C_2 = \frac{1}{2k'_2 C_e} (4k'_1 C_1 - 2k'^2_1 - 8k'_1 k'_2 C_e - 4C_1 C_e k'_2 - 4C_e^2 k'^2_2)^{1/2}$$

The adopted solution is given by relation (13) because C_2 constant should have a positive value.

If Q_1 and Q_2 denote the heat quantities released, respectively, by hemihydrate dissolution and dihydrate precipitation reactions, then:

$$\frac{dQ_1}{dt} = V \Delta_{\text{dis}} H k'_1 (C_e - [\text{Ca}^{2+}]) \quad \text{and}$$

$$\frac{dQ_2}{dt} = V \Delta_{\text{pp}} H k'_2 [\text{Ca}^{2+}]^2$$

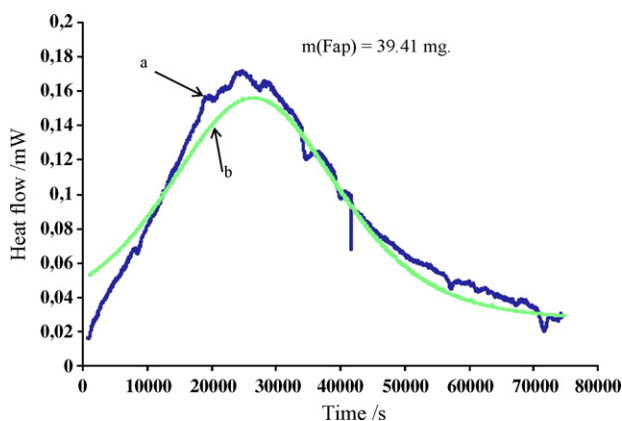


Fig. 5. An example of iteration result of the Eq. (16) and thermogenesis for the second peak. (a) Recorded peak. (b) Calculated curve.

where V is the volume of the reactional medium; $\Delta_{\text{dis}}H$ and $\Delta_{\text{pp}}H$ are the molar enthalpies of hemihydrate dissolution and dihydrate precipitation reactions, respectively.

The total heat quantity (Q) measured during the experiment is the sum:

$$Q = Q_1 + Q_2$$

and so:

$$\frac{dQ}{dt} = V\Delta_{\text{dis}}Hk'_1(C_e - [\text{Ca}^{2+}]) + V\Delta_{\text{pp}}Hk'_2[\text{Ca}^{2+}]^2 \quad (15)$$

The final heat flow expression is expressed as:

$$\begin{aligned} \frac{dQ}{dt} = & V\Delta_{\text{dis}}Hk'_1 \left[C_e - \frac{1}{2k'_2} - k'_1 + C_1th \left(\frac{C_1}{2}t + \ln C_2 \right) \right] \\ & + V\Delta_{\text{pp}}Hk'_2 \left[\frac{1}{2k'_2} \left(-k'_1 + C_1th \left(\frac{C_1}{2}t + \ln C_2 \right) \right) \right]^2 \end{aligned} \quad (16)$$

The iteration of the heat flow expression (16) includes 6 parameters: $\Delta_{\text{dis}}H$, $\Delta_{\text{pp}}H$, k'_1 , k'_2 , C_e and C_2 ; we have included the C_2 parameter because of the complexity of its expression. Fig. 5 shows an example of calculated and recorded curves obtained for 39.41 mg Fap. For the other masses of Fap, coincidence is similar and the whole iteration values of k'_1 , k'_2 , $\Delta_{\text{dis}}H$, $\Delta_{\text{pp}}H$, C_e and C_2 pertain to the intervals: $[4.15 \times 10^{-5}; 5.00 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}]$, $[1.45 \times 10^{-3}; 1.99 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}]$, $[11.90; 12.30 \text{ kJ mol}^{-1}]$, $[-25.10; -24.90 \text{ kJ mol}^{-1}]$, $[3.12 \times 10^{-4}; 3.27 \times 10^{-4} \text{ mol L}^{-1}]$ and $[31.01; 59.33]$, respectively. It can be noticed that the mean iteration value of $\Delta_{\text{dis}}H$ ($+12.10 \text{ kJ mol}^{-1}$) is close to the opposite of the enthalpy of precipitation of hemihydrate

from Ca^{2+} and SO_4^{2-} , calculated above ($-11.18 \text{ kJ mol}^{-1}$), and the enthalpy of precipitation of the dihydrate deduced iteratively ($-25.00 \text{ kJ mol}^{-1}$) is close to the enthalpy previously calculated for reaction VII ($-24.18 \text{ kJ mol}^{-1}$). Moreover the sum $\Delta_{\text{dis}}H + \Delta_{\text{pp}}H = -25.00 + 12.10 = -12.90 \text{ kJ mol}^{-1}$ is close to the enthalpy of the second peak deduced by integrating the second peak ($-13.06 \text{ kJ mol}^{-1}$). Besides the solubility mean value of the hemihydrate at 55°C , deduced iteratively ($C_e = 3.27 \times 10^{-4} \text{ mol L}^{-1}$) is in the same order of magnitude of the one deduced by extrapolating the results of Nancollas et al. [12] taking into account the sulfate concentration in the acid mixture ($1.36 \times 10^{-4} \text{ mol L}^{-1}$), and the mean value of C_2 constant (46.23) deduced from iteration, is of the order of magnitude of that calculated according to its expression above, taking into account the mean values of the other parameters ($C_2 = 58.74$).

Transformation of hemihydrate into dihydrate has been studied by many authors using different experimental techniques: conductivity measurements [8], time resolution X-ray powder diffraction using a synchrotron radiation [9], ICP spectroscopy analysis and BET [10]. But only Witkamp et al. [10] have proposed a mathematical model comprising a first order process for the hemihydrate dissolution and a second order one for the growth of dihydrate. Our results confirm these values for the order rates.

As a concluding remark, most of the papers dealing with transformation of hemihydrate into dihydrate operated discontinuously by filtration and analysis while calorimetry enables to follow that transformation in situ without any interruption.

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