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THEORETICAL INTERPRETATION OF THE EXISTENCE AT 35°C OF AN ABSOLUTE MAXIMUM OF THE HYDRATION RATE OF CALCIUM SULFATE HEMIHYDRATE

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ABSTRACT

Isothermal calorimetric measurements of β-$CaSO_4 \cdot 0.5\ H_2O$ hydration by liquid water between 5 and 50°C show that the hydration rate passes through a maximum at about 35°C. This phenomenon is explained theoretically by consideration of the crystallization and dissolution constant rates and the solubility diagram.

It results from the fact that the usual increase of rate constants with temperature is associated with a variation, in opposite directions of the positive difference of solubility between the two salts. This phenomenon is certainly general and may be found in the study of other pairs of salts.

INTRODUCTION

In previous investigations[1, 2], the variation of hydration rate of hemihydrated calcium sulfate with temperature was studied by isothermal calorimetry. It was shown that the time, t_m, corresponding to the maximum of thermal flow, Φ_m, related to the hydration reaction passes through a minimum at about 35°C and that the values of Φ_m, which are directly proportional to the hydration rates, pass through a maximum at the same temperature (Fig. 1).

In a recent paper[3], a kinetic interpretation based on the fact that the total reaction may be represented by two simultaneous phenomena has been proposed

dissolution: solid 1 (hemihydrate) + water → solution
recrystallization: solution → solid 2 (dihydrate)

This interpretation is based on the proved approximation of the equality of the dissolution rate of hemihydrate and the crystallization rate of gypsum (dihydrate).

A close examination of experimental results[4, 5] with regard to the kinetics of dissolution of crystallized salts in water allows the relative variation of a characteristic dimension r (initially r_0) of crystals to be expressed in the form

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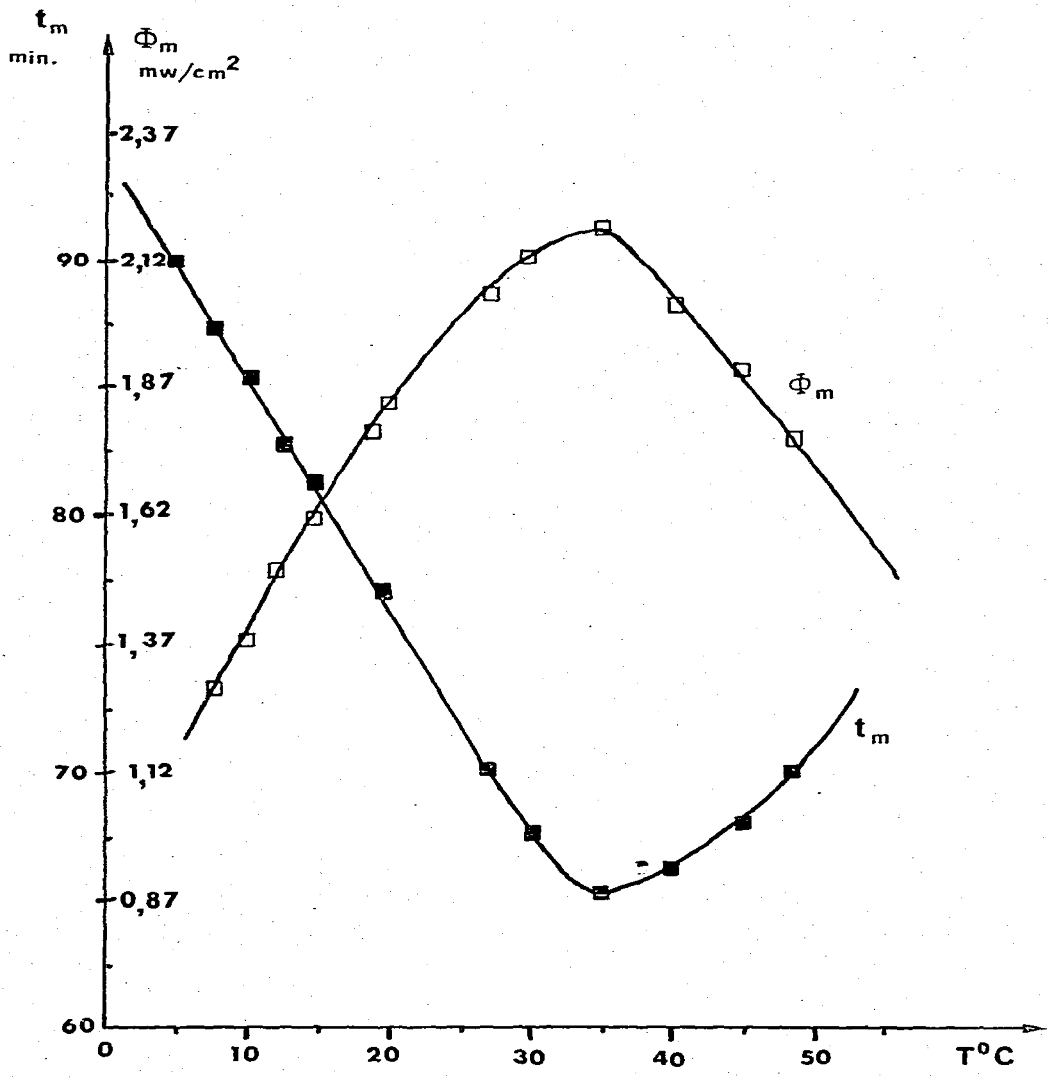

Fig. 1. ▨, Variation of t_m with temperature. ☐, Variation of the maximum of the thermal flow, Φ_m, between 5 and 50°C.

$$\frac{dr}{r_0} = -k_1(C_D^0 - C_D)^m\,dt$$

where k_1 is the rate constant which depends on the temperature T, $C_D^0 - C_D$ is the difference, at the temperature T, between the concentration at saturation C_D^0 and the concentration C_D at time t, of the dissolved salt, and m is an exponent (generally an integer).

The expression for r versus time is obtained by integration of the above expression.

$$r = r_0\left[1 - k_1\int_{t_0}^{t}(C_D^0 - C_D)^m\,dt\right]$$

The volume v of a grain at time t may then be expressed as

$$v = v_0 \left[1 - k_1 \int_{t_0}^{t} (C_D^0 - C_D)^m \, dt\right]^{p_1}$$

where v_0 is the initial volume at time t_0.

If we call α the global degree of conversion of the hemihydrate into gypsum, the above relation is written

$$1 - \alpha = \left[1 - k_1 \int_{t_0}^{t} (C_D^0 - C_D)^m \, dt\right]^{p_1}$$

The expression for the dissolution rate

$$V_D = p_1 k_1 (C_D^0 - C_D)^m (1 - \alpha)^{(p_1 - 1)/p_1}$$

is derived and by analogy the rate of crystallization is written

$$V_C = p_2 k_2 (C_D - C_D^F)^n \alpha^{(p_2 - 1)/p_2}$$

where C_D^F is the saturation concentration at temperature T of the crystallizing salt.

In the particular case, C_D° is the saturation concentration of the hemihydrate in the aqueous solution used for hydration at time t_0, and C_D^F is the concentration of the same solution when the hydration reaction can be considered as completed.

The conversion rate for which the rate is maximum is then, as a first approximation

$$\alpha_{max} = \frac{mp_1(p_2 - 1)}{mp_1(p_2 - 1) + np_2(p_1 - 1)}$$

independent of the temperature at which the reaction takes place[3].

This remarkable property of α_{max} allows the maximum of the rate of the hydration reaction for hemihydrated calcium sulfate, $CaSO_4 \cdot 0.5\ H_2O$, into gypsum, $CaSO_4 \cdot 2H_2O$, to be determined at 35 °C.

THEORETICAL INTERPRETATION

Under the above conditions, the maximal rate of the gypsum formation reaction is written

$$V_{max} = p_2 k_2 (\bar{C}_D - C_D^F)^n \alpha_{max}^{(p_2 - 1)/p_2}$$

$\bar{C}_D$ being the concentration at maximum rate. Thus, the maximal rate depends of the temperature only through the product of k_2 and $(\bar{C}_D - C_D^F)^n$.

The existence of an absolute maximum of the maximal rate V_{max} for a temperature T_{max} is given by

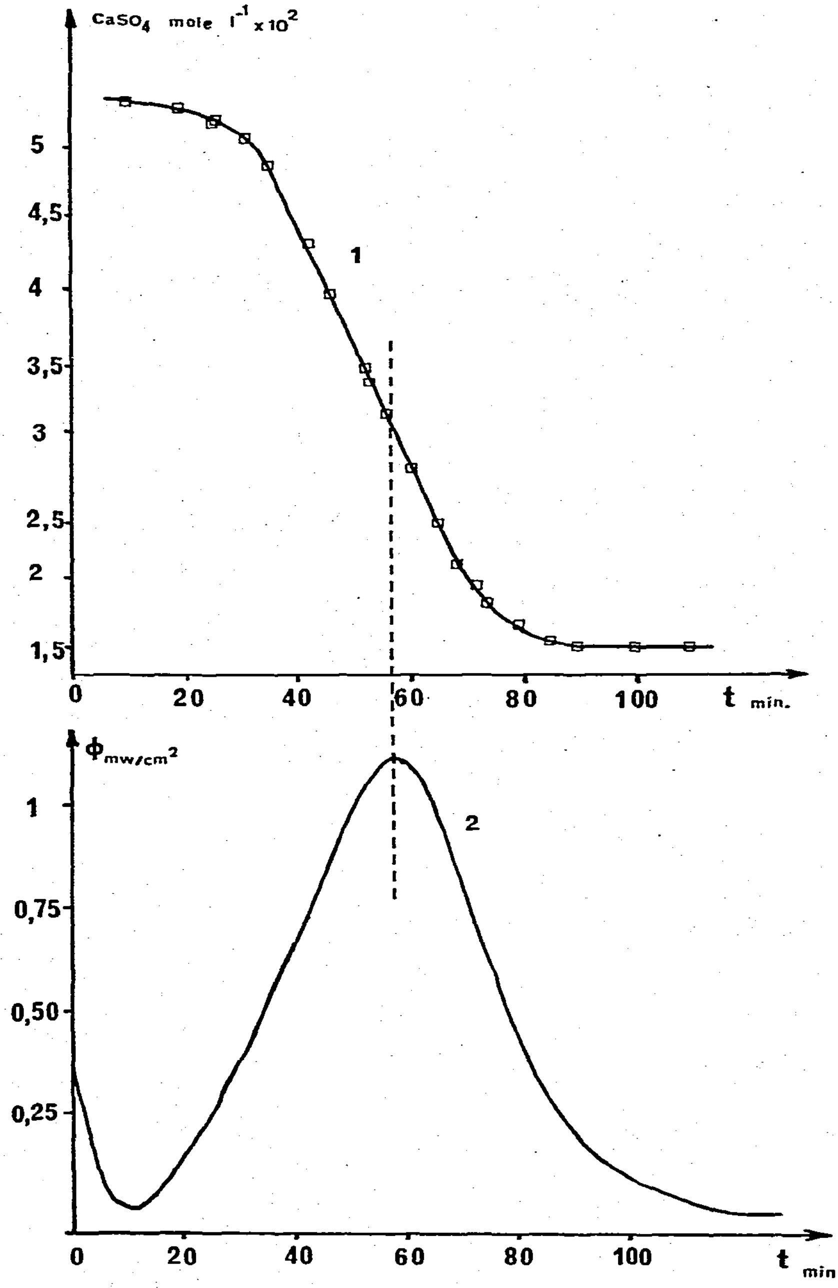

Fig. 2. 1, Variation of the concentration of CaSO4 in the aqueous solution with time during hydration. 2, Variation of the corresponding thermal flow with time.

$$\frac{d}{dT}\left[k_2(\bar{C}_D - C_D^F)^n\right] = 0$$

Let us assume that k_2 obeys the Arrhenius law, $k_2 = k_{o_2} \exp(-E_c/RT)$, where E_c is the apparent activation energy of the crystallization reaction and k_{O_2} a factor appreciably independent of T and let us write, according to the shape of the experimental curves (Fig. 2) of the variation of the concentration of calcium sulfate in solution and of the reaction rate versus time

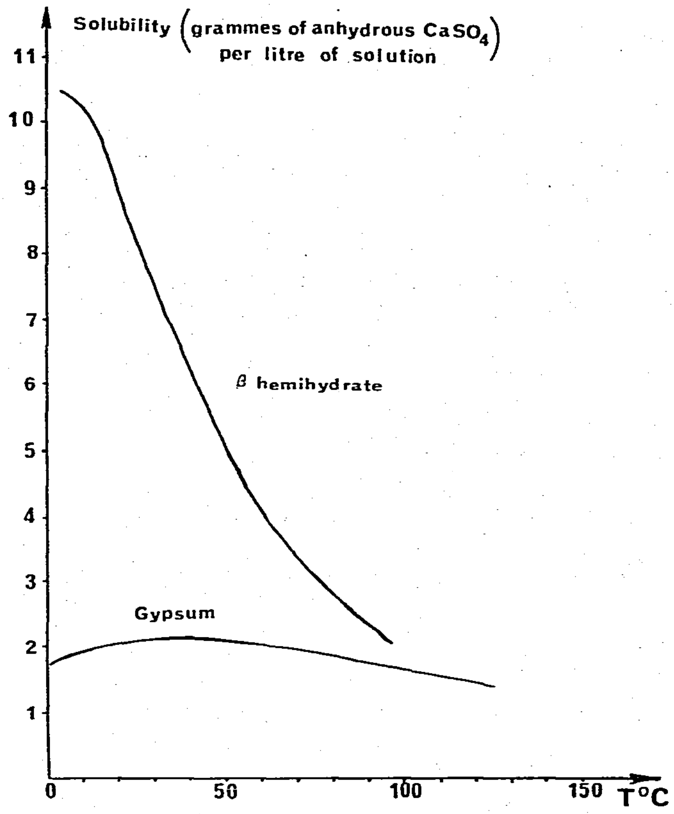

Fig. 3. Solubility curves of calcium sulfates in water.

$$\bar{C}_D - C_D^F = (C_D^0 - C_D^F)(1 - \alpha_{max})$$

The condition of existence of the maximum becomes

$$\frac{d}{dT}[\exp(-E_c/RT)(C_D^0 - C_D^F)^n] = 0$$

and, referring to the hemihydrate and gypsum solubility curves (Fig. 3)[6, 7] it can be seen that C_D^F is practically independent of temperature compared with C_D^o, the variation of which is best expressed for temperatures between 20 and 80°C, by

$$C_D^0 = C_{298}^0 \exp\left[\frac{\Delta H^0}{2R}\left(\frac{1}{298} - \frac{1}{T}\right)\right]$$

ΔH° is comparable to an apparent dissolution heat of hemihydrate under a pressure of one atmosphere.

This enthalpy variation is supposed to depend only very little on temperature in the range 20–80°C.

One calculates $\Delta H^\circ = -8.3$ kcal mole^{-1} (or -35.0 kjoule mole^{-1}).

$$\frac{d}{dT}\left[\exp(-E_c/RT)\left\{\exp\left[\frac{\Delta H^0}{2R}\left(\frac{1}{298} - \frac{1}{T}\right)\right] - \frac{C_D^F}{C_{298}^0}\right\}^n\right] = 0$$

Let us write $C_D^F/C_{298}^\circ = q$, practically independent of T. The temperature of the maximum is the solution of the equation

$$\frac{\mathrm{d}}{\mathrm{d}T}\left\{\exp\left[-\frac{E_c}{nRT}+\frac{\Delta H^0}{2R}\left(\frac{1}{298}-\frac{1}{T}\right)\right]-q\exp\left[-\frac{E_c}{nRT}\right]\right\}^n=0$$

After derivation, one finds the following relation between E_c and T_{max} which corresponds actually to a maximum

$$E_c=-\frac{n\,\Delta H^0/2}{1-q\exp\left[-\frac{\Delta H^0}{2R}\left(\frac{1}{298}-\frac{1}{T}\right)\right]}$$

Using the values $\Delta H^\circ = -8.3$ kcal (or -35.0 kJoule), $q \simeq \frac{1}{4}$ and $T_{max} = 308$ K in the former equation, we find finally $E_c = 6\,n$ kcal mole^{-1} (or $25\,n$ kJoule mole^{-1}). In the case of a crystallization process, governed by diffusion, we generally use $n = 1$. If the process is governed by interactions between water and dihydrate, we use $n = 2$. So, for a diffusional process $E_{c_1} \approx 6$ kcal mole^{-1} (or 25 kJoule mole^{-1}) and for a non-diffusional process, $E_{c_2} \approx 12$ kcal mole^{-1} (or 50 kJoule mole^{-1}).

Values found in the literature[8-10] are in good agreement for non-diffusional processes: $E_{c_2} \approx 15$ kcal mole^{-1} (or 63 kJoule mole^{-1}).

Conversely, using the values of E_c we could have calculated T_{max}. So, we are in right to consider the existence of a maximum rate at 35 °C resulting from variations in the opposite direction of the rate constant which increases, and the concentration difference $C_D^\circ - C_D^F$ which decreases as temperature increases.

CONCLUSION

By means of a simple kinetic model, it has been shown that the existence of a maximal rate at 35 °C of the hydration reaction of hemihydrated calcium sulfate is explained by the usual increasing of rate constants with temperature, associated with a variation in the opposite direction of the positive difference of solubility between the two salts.

This phenomenon may be observed in other cases of hydration including other pairs of salts.

REFERENCES

1 M. Murat and E. Karmazsin, in I. Buzas (Ed.), *Thermal Analysis. Proc. 4th ICTA, Budapest, July 1974*, Vol. 3, Akademiai Kiado, Budapest, 1975, pp. 635–645.
2 M. Murat and E. Karmazsin, in M. Murat and M. Foucault (Eds.), *Proc. Int. RILEM Symp., St-Rémy-les-Chevreuse, France, May 25–27, 1977*, pp. 217–36.
3 C. Comel, E. Karmazsin and M. Murat, *Giornata di Calorimetria et di Analisi Termica, Turin, June 28–30, 1978*.
4 A. L. Jones, *Trans. Faraday Soc.*, 59 (1963) 2355.
5 C. H. Bovington and A. L. Jones, *Trans. Faraday Soc.*, 66 (1970) 2088.
6 L. Chassevent, *Ann. Chim.*, 6 (1926) 244.

7 W. H. Power and B. Fabuss, *J. Chem. Eng. Data*, 9 (1964) 437.
8 Sung Tsuen Liu and G. H. Nancollas, *J. Cryst. Growth*, 6 (1970) 281.
9 B. R. Smith and F. Sweett, *J. Colloid Interface Sci.*, 37 (1971) 612.
10 G. H. Nancollas, M. M. Reddy and F. Tsai, *J. Cryst. Growth*, 20 (1973) 125.