PHYSICAL CHEMISTRY

V. B. RATINOV, T. I. ROZENBERG, and N. M. RUBININA

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. B. RATINOV, T. I. ROZENBERG, and N. M. RUBININA

INVESTIGATION OF THE KINETICS OF CRYSTALLIZATION OF CALCIUM HYDROSULFOALUMINATE

(Presented by Academician P. A. Rebinder, 19 VI 1961)

The work is devoted to finding the dependence of the crystallization rate of the high-sulfate form of calcium hydrosulfoaluminate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$) on supersaturation in the absence of externally introduced seed, and to determining the values of its free surface energy σ at the boundary with the solution. Supersaturation was produced by pouring the corresponding solutions into an aluminum sulfate solution while stirring it at a constant rate. Two independent series of experiments were carried out: in the first, calcium hydrosulfoaluminate was synthesized from aluminum sulfate, the concentration of which was constant ($C = 10.8 \cdot 10^{-4}$ mol/l), and calcium hydroxide hydrate, the concentration of which varied within the range from $7.37 \cdot 10^{-3}$ to $11.8 \cdot 10^{-3}$ mol/l. In the second series of experiments, aluminum sulfate, calcium hydroxide hydrate, and calcium sulfate were mixed, the concentration of the latter two compounds being constant ($C_{Ca(OH)2} = 7.8 \cdot 10^{-3}$ mol/l, $C_{CaSO4} = 8.03 \cdot 10^{-3}$ mol/l), while the concentration of aluminum sulfate was varied within the range from $3.5 \cdot 10^{-4}$ to $9.5 \cdot 10^{-4}$ mol/l. The starting reagents were "chemically pure" and "analytically pure" ; before the experiments, the solutions were filtered through a glass filter No. 4; the experiments were conducted in a nitrogen atmosphere at 20°. The concentration of aluminum ions was determined colorimetrically with the aid of the reagent stilbazo ([1]), and the concentration of the remaining ions by a volumetric method ([2]). The solid phase was identified from X-ray, petrographic, thermographic, and chemical analysis data ([3]). In each of the two series of experiments, the crystallization kinetics of calcium hydrosulfoaluminate was studied at no fewer than 4-5 supersaturations by periodic sampling and analysis.

The data on the crystallization kinetics of calcium hydrosulfoaluminate were processed in two ways. In the first, theoretical investigations ([4,5]) were taken into account.

In work ([4]) it was shown that, for well-dissociated salts, the degree of supersaturation in the Gibbs–Volmer equation must be replaced by the ratio $\Pi\Pi/\Pi P$, and the equation itself written in the form:

$$\alpha = A' \exp\left\{-\frac{4\gamma v^2 \sigma^3}{(kT)^3 \ln^2(\Pi\Pi/\Pi P)}\right\}, \tag{1}$$

where $\Pi\Pi$ is the product of the activities of the ions introduced into the solution; ΠP is the solubility product of the new formations; v is the molecular volume of the new phase; γ is the crystal shape factor; k is Boltzmann' s constant; T is the absolute temperature.

In calculations on the crystallization of calcium hydrosulfoaluminate, the activities were replaced by concentrations; this introduced a small error into the value of the final ratio

$$\frac{\Pi\Pi}{\Pi P} \simeq \frac{C_{\mathrm{Ca}}^{6} C_{\mathrm{Al}}^{2} C_{\mathrm{SO4}}^{3}}{C_{\mathrm{Ca0}}^{6} C_{\mathrm{Al0}}^{2} C_{\mathrm{SO4}}^{3}}. \tag{2}$$

Analysis (^{4,5}) shows that the probability of formation of nuclei of a new phase per unit volume per unit time is

$$\alpha \sim \frac{1}{\tau^4}; \tag{3}$$

here τ is the duration of the induction period, for which in all cases we took the time from the start of the experiments to the moment when the concentration of aluminum ions decreased by the amount $C = 4 \cdot 10^{-5}$ g-ion/l (see Fig. 1). Then, in accordance with equation (1), the average value of σ is determined from a graph constructed from the experimental data in the coordinates $\lg \frac{1}{\tau^4}$ $-\frac{1}{\lg^2(\Pi\Pi/\Pi P)}$ (all the other quantities entering this equation, except the pre-exponential factor A', are known for calcium hydrosulfoaluminate). The value of σ determined from the first series of experiments proved to be 61 erg/cm^2; for the second series of experiments $\sigma = 57$ erg/cm^2; the course of the calculations is shown in Table 1.

Table 1

Data for determining the free surface energy of calcium hydrosulfoaluminate at the crystal–solution boundary (series II)

Indicators	Experiment no. 1	Experiment no. 2	Experiment no. 3	Experiment no. 4
$C_{\mathrm{Al}} \cdot 10^3$ g-ion/l	1.90	1.42	1.02	0.70
$C_{\mathrm{SO_4}} \cdot 10^3$ g-ion/l	10.88	10.16	9.53	9.08
$\frac{\Pi\Pi}{\Pi P} \cdot 10^{-15}$	4.61	2.10	0.90	0.365
τ, min.	5.0	8.0	12.0	18.0
A, min.	0.097	0.12	0.15	0.18

The second method for calculating the value of σ from experimental data is based on the use of the theoretical dependence of the kinetics of crystal growth in the diffusion region on the relative supersaturation $(C_\tau - C_0)/(C_p - C_0) = B$, the applicability of which to cases of crystallization of calcium hydrosulfoaluminate was demonstrated in (7).

In integral form the equation is

$$A\tau = \ln \frac{1 + \sqrt[3]{1-B} + \sqrt[3]{(1-B)^2}}{1 - \sqrt[3]{1-B}} + \sqrt[3]{3} \left\{ \operatorname{arctg} \frac{\sqrt[3]{1-B} + 1/2}{\sqrt{3}/4} - \frac{\pi}{6} \right\}, \qquad (4)$$

where $A\tau$ is dimensionless time; C_p is the initial concentration of the introduced substance; C_0 is the equilibrium solubility of the new formation ($C_0 = 9 \cdot 10^{-5}$ mol/l); C_τ is the concentration of the substance in solution at time τ;

$$A = 3K \sqrt[3]{N\rho\gamma}\,(C_p - C_0)^{2/3}. \qquad (5)$$

Here K is a constant related to the diffusion coefficient D; N is the number of crystals; ρ is their density.

Since in the different experiments of each series the changes in the quantities D and $C_p - C_0$ are comparatively small, while the value of N changes very substantially (5,6), equation (5) can be replaced by the approximate dependence

$$A \sim N^{1/3}. \qquad (6)$$

But $N^{1/3} \sim \alpha^{1/4}$, whence finally

$$\alpha \sim A^4. \qquad (7)$$

The value of α was determined from equation (1). This made it possible to calculate the average value of σ from a graph constructed in the coordinates $\lg A^4 – \frac{1}{\lg^2(\Pi\Pi/\Pi P)}$, with the value of A in each experiment found by ···

processing the descending branch of the experimental crystallization kinetic curve in accordance with equation (4). The results obtained are presented in Table 1; the approximate value of σ calculated with their aid proved to be 47 erg/cm^2 and, taking into account the assumptions adopted, is in satisfactory agreement with the data given above, calculated by another method.

Fig. 1. Kinetics of crystallization of calcium hydrosulfoaluminate as a function of the change in the concentration of calcium hydroxide hydrate (series I).
1 –$11.8 \cdot 10^{-3}$ mol/l; 2 –$9.44 \cdot 10^{-3}$ mol/l; 3 –$8.24 \cdot 10^{-3}$ mol/l; 4 –$7.66 \cdot 10^{-3}$ mol/l; 5 –$7.35 \cdot 10^{-3}$ mol/l $Ca(OH)_2$

Fig. 1. Kinetics of crystallization of calcium hydrosulfoaluminate as a function of the change in the concentration of calcium hydroxide hydrate (series I). 1 – $11.8 \cdot 10^{-3}$ mol/l; 2 –$9.44 \cdot 10^{-3}$ mol/l; 3 –$8.24 \cdot 10^{-3}$ mol/l; 4 –$7.66 \cdot 10^{-3}$ mol/l; 5 –$7.35 \cdot 10^{-3}$ mol/l $Ca(OH)_2$

Figure 1: Fig. 1. Kinetics of crystallization of calcium hydrosulfoaluminate as a function of the change in the concentration of calcium hydroxide hydrate (series I). 1 –$11.8 \cdot 10^{-3}$ mol/l; 2 –$9.44 \cdot 10^{-3}$ mol/l; 3 –$8.24 \cdot 10^{-3}$ mol/l; 4 –$7.66 \cdot 10^{-3}$ mol/l; 5 –$7.35 \cdot 10^{-3}$ mol/l $Ca(OH)_2$

Determination of the value of σ without replacing, in the Gibbs-Folmer formula, the degree of supersaturation C_p/C_0 by $\Pi\Pi/\Pi P$ would lead, for calcium hydrosulfoaluminate, to an underestimated value of the free surface energy at the crystal-solution boundary (mean $\sigma \approx 6$ erg/cm^2).

Scientific Research Institute
of Reinforced-Concrete Products, Building Structures, and
Nonmetallic Materials

Received
2 VI 1961

REFERENCES CITED

1. V. I. Kuznetsov, G. G. Karanovich, D. A. Drapkin, *Zav. lab.*, **16**, No. 7, 787 (1950).
2. T. I. Rozenberg, V. B. Ratinov, *Collection of Proceedings of the Research Institute of Reinforced Concrete*, issue 1, 36 (1957).
3. I. O. Gracheva, A. Ya. Vikulin, *Proceedings of the Research Institute of Asbestos Cement*, issue 11, 91 (1961).
4. V. B. Ratinov, O. M. Todes, *DAN*, **132**, No. 2, 402 (1960); *Collection of Proceedings of the Research Institute of Reinforced Concrete*, issue 4, Gosstroiizdat, Moscow, 154 (1961).
5. O. M. Todes, *Problems of Kinetics and Catalysis*, Publishing House of the Academy of Sciences of the USSR, **7**, 91 (1949).
6. S. Z. Roginskii, O. M. Todes, *Izv. AN SSSR, OKhN*, 1940, 331.
7. V. B. Ratinov, T. I. Rozenberg, N. M. Rubinina, G. G. Melent' eva, *DAN*, **136**, No. 6 (1961).