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THE DIGESTION OF SYNTHETIC GIBBSITE①

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ABSTRACT The Dissolution process of synthetic gibbsite in sodium hydroxide solution was investigated by isothermal calorimetry in a conduction-type automatic calorimeter. The experiment was carried out at 75~100 ℃. The reagent used for dissolution was 4.19~7.37 mol/L NaOH solution. The heat of the digestion of synthetic gibbsite was measured. By analyzing the effect of temperature and concentration on dissolution rate, a mathematical model for dissolution process was derived. The experimental result showed that the rate determining step is a chemical reaction rather than diffusion. A first-order dependence on the concentration of sodium hydroxide was observed. The apparent activation energy is 76.85 kJ/mol, which is in fair agreement with that in references.

Key words synthetic gibbsite digestion heat effect kinetic behavior

1 INTRODUCTION

Gibbsite-a trihydrate aluminium oxide is the most important one of three naturally occurring forms of aluminium oxide in bauxites. Recently, it also has been found in China.

For improving the digestion of gibbsite, it is important to have the knowledge of the kinetics of the dissolution of gibbsite in NaOH solution. Tatsubiko[1], Lunquist[2], Glastonbury[3], Scotford[4], and Roach[5] found that the rate-determining step of the dissolution reaction of gibbsite was chemical reaction. Абрамов В Я[6], Райзман В Л[7] considered that the dissolution was controlled by diffusion step. The results of Wahnsiedler[8], Borntrager[9] and Yun Anjun[10] showed that the rate-determining steps were both chemical reaction and diffusion. So far, no universal kinetic model was obtained. In fact, it was difficult to accomplish this purpose. There are too many facts affecting the dissolution process, such as variety of ores, size of particles, temperature, liquor concentration, impurities, stirring velocity, composition and so on.

The earlier researchs were usually carried out in autoclave. Gibbsite sample and NaOH solution of the desired concentration were added into each reactor and brought to desired temperature in a thermostat bath. At regular interval, solution samples were withdrawn and analysed for aluminium content. From 6 ~8 such samplings and analysings, the initial extraction rate was determined. Obviously, this method was discontinuous for operating and analysing.

At higher temperature, the technique was modified to allow a continuous flow of NaOH solution through the reactor[9]. Electrical conductivity measurement enabled the continuous monitoring of the aluminium concentration in the reactor. Initial extraction rates were calculated from the conductivity-time data.

Then non-isothermal analysis method[10] was a useful and good method for the investigation of kinetics. But it is complicated for data process.

Isothermal calorimetry could avoid the shortage of the method using high-pressure bomb(autoclave) and take some advantage of

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non-isothermal calorimetric method. It was convenient to measure the reaction continuously. The thermokinetic curve could not only record the whole kinetic procedure and provided more kinetic information, but also provided a measurement of the heat of dissolution, in a given time interval, and gived an accurate representation of kinetics of reaction.

2 PRINCIPLE

In general, all phenomena of a physical, chemical or biological nature are accompanied by thermal effects. The magnitude of heat effect is proporational to the decrease of a reactant or the increase of a product. Based on this, if a instantaneous heat effect could be measured, a kind of simple way would be found for studying chemical reaction kinetics.

When a chemical reaction is taking place in a conduction calorimeter, a thermokinetic curve is recorded(as shown in Fig. 1).

According to Calvet and Part[11], the rate of heat production, $d\theta/dt$, could be calculated using Tian's equation:

$$\frac{d\theta}{dt} = K(\Delta + \tau \frac{d\Delta}{dt}) \tag{1}$$

where Δ is the peak height at time t; K and τ are the apparatus constant and time-constant of the calorimeter, respectively.

After integration, the following equation is obtained:

$$Q = K(a + \tau\Delta) \tag{2}$$

and $Q_\infty = KA$ (3)

where Q is the heat produced before time t; Q_∞ is the total heat effect; a is the peak area before time t; A is the total area under the curve.

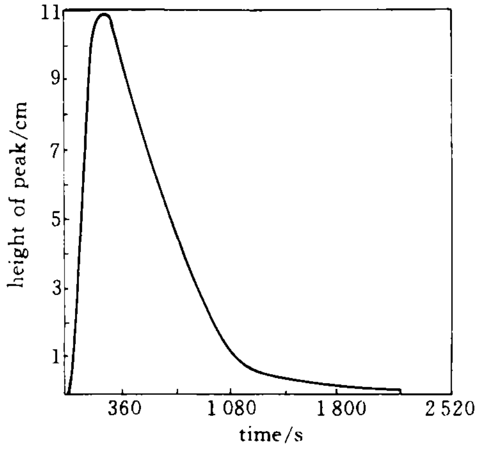

Fig. 1 Thermokinetic curve for digestion of synthetic gibbsite

According to thermochemical kinetics, the heat flux is proporational to the reaction rate.

$$\frac{d\alpha}{dt} = \frac{1}{Q_\infty} \cdot \frac{dQ}{dt} \tag{4}$$

$$\alpha = \frac{W_0 - W}{W_0} \tag{5}$$

where α is the reacted fraction and W_0, W are the weight of reactant at initial time and at time t, respectively.

Combining equation (4) and (5) with equation (1), (2), (3), we obtain:

$$\frac{d\alpha}{dt} = \frac{\Delta + \tau \frac{d\Delta}{dt}}{A} \tag{6}$$

After integration, $\alpha = \frac{a + \tau\Delta}{A}$ (7)

The values of K and τ could be easily determined by calibration method. Heat effect Q could be easily calculated by equation(2). α, $d\alpha/dt$ could be obtained from the measured curve $\Delta(t)$ and the differentiated measured curve $d\Delta/dt(t)$ by simple algebraic calculations.

In present investigation, the test samples were synthetic gibbsite powder, it could be completely dissolved in sodium hydroxide solution without solid product layer formed.

Stirring was necessary in our experiment process. The diffusion resistance could be neglected. The expereiments were carried out in nonequalibrium conditions. Therefore we assumed that the rate-determining step in the digestion process was controlled by irreversible chemical reaction. According to chemical reaction kinetics, the rate equation of a first-order irreversible reaction could be derived as:

$$\frac{d\alpha}{dt} = K' \cdot 4\pi r_0^2 \cdot N_0 \cdot (R' - \alpha)(1 - \alpha)^{2/3} \tag{8}$$

and $R' = \frac{C_0^0 V}{W_0/M}$

where r_0 is the initial radius of the particles; N_0 is the number of particles; C_0^0 is the initial concentration; V is the volume of solution; M is the molar mass of particle.

For second-order irreversible reaction, the rate equation could be derived as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K' \cdot 4\pi r_0^2 \cdot N_0 (R' - \alpha)^2 \cdot (1 - \alpha)^{2/3} \cdot \frac{W_0}{MV} \tag{9}$$

For n -order irreversible reaction, the rate equation could be presented as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K' \cdot 4\pi r_0^2 \cdot N_0 (R' - \alpha)^n \cdot (1 - \alpha)^{2/3} \cdot \left(\frac{W_0}{MV}\right)^{n-1} \tag{9}$$

or
$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K \cdot (R' - \alpha)^n \cdot \left(\frac{W_0}{MV}\right)^{n-1} \cdot (1 - \alpha)^{2/3} \tag{10}$$

where $K = K' \cdot 4\pi r_0^2 \cdot N_0$

In logarithmic form:

$$\ln\left[\frac{\mathrm{d}\alpha}{\mathrm{d}t}(1 - \alpha)^{-\frac{2}{3}}\right] = \ln K + n\ln\left[(R' - \alpha)\frac{W_0}{MV}\right] - \ln\frac{W_0}{MV} \tag{11}$$

With a linear plot of $\ln\left[\frac{\mathrm{d}\alpha}{\mathrm{d}t}(1 - \alpha)^{-\frac{2}{3}}\right]$ to $\ln\left[(R' - \alpha)\frac{W_0}{MV}\right]$, R and n could be calculated from the intercept and slope of the plot.

3 EXPERIMENT

3.1 *Reagents and Apparatus*

The test sample-gibbsite was precipitated from an aluminate solution by adding pure gibbsite crystal seed. The deposited crystals were washed repeatedly with distilled water until supernatant liquid became neutral, ensuring the removal of alkali. Analysis, after drying over phosphorous pentoxide, gave 64.25% Al_2O_3 (theoretical value 65.4%), and 0.2% Na_2O. The sample was confirmed as pure gibbsite by X-ray diffraction.

The sodium hydroxide used was of analytical pure grade. Standardization with potassium hydroxide phthalate gave the concentration of NaOH solution as 4.19, 5.11, 5.93, 6.33, 7.19 and 7.37 mol/L, respectively.

The heat conduction type automatic calorimeter is shown in Fig. 2. The sample cell, shown in Fig. 3, was used to keep the solid (gibbsite) separate from NaOH solution until the desired temperature was reached. The cell containing separated NaOH solution and gibbsite was placed into the calorimeter at room temperature.

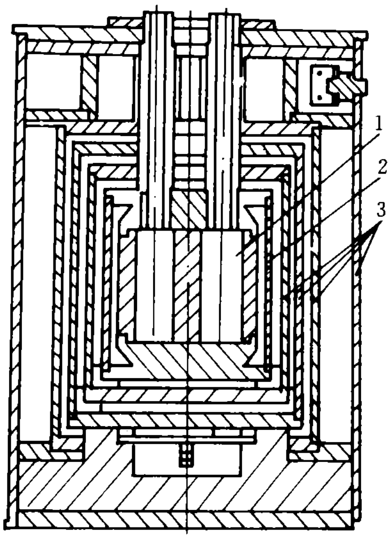

Fig. 2 Heat conduction calorimeter

1—the tube for setting calorimetric elements;
2—metal block, of good conductivity;
3—isothermal jacket

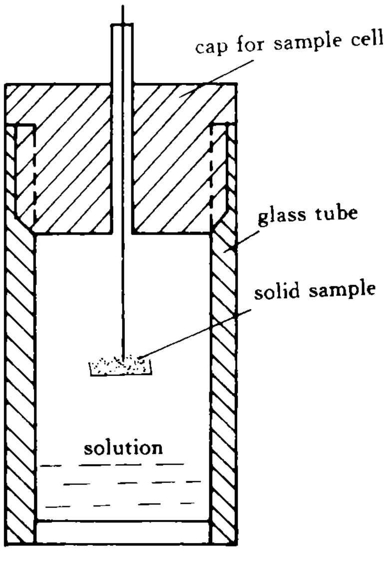

Fig. 3 Sample cell

3. 2 *Determination of Calorimeter Constant K and Time Constant τ*

When a constant heat power W was generated in the sample-cell without compensation, a deviation Δ was resulted on the recorder. Once the steady state was established (see Fig. 4), the deviation became constant ($d\Delta/dt = 0$). In this condition, equation (1) reduced to

$$W = \frac{dQ}{dt} = K\,\Delta \qquad (12)$$

To measure the values of K and τ, a constant heating power was given at time A from Joule effect unit. The curve $ABCD$ was traced out, becoming parallel to the time axis in CD. The constant deviation Δ was the height as in the Fig. 4.

$$K = \frac{W}{\Delta} = \frac{W}{\Delta_{Aa}} \qquad (13)$$

The part DE of Fig. 4 represented that the recorder deflection returned to the experimental zero after cutting off the power W in the sample cell.

Since no heat was produced in the cell, nor was any compensation made during the period DE, the equation (1) became:

$$0 = K[a + (0 - \Delta_0)\tau]$$

$$\tau = \frac{a}{\Delta_0} = \frac{a}{\Delta_{Dd}} \qquad (14)$$

where a was the shade area DdE and Δ_0 was the deviation, $D\,d$ was at the instant of suppression of the power W.

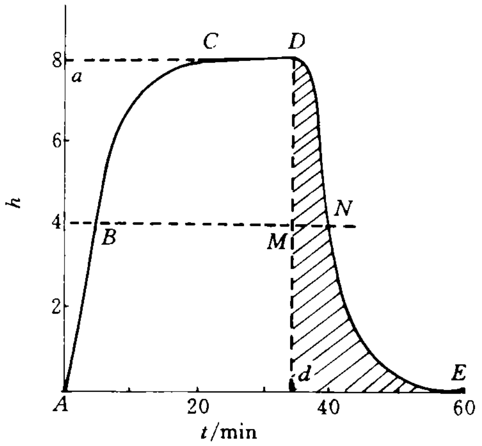

Fig. 4 Measurement of calorimeter constant and time constant

A dissolution experiment of potassium chloride (guaranteed grade, 99. 99% KCl) was performed at 25 ℃ to examine the validity of this Joule effect calibration method, the result was 1. 126 J/cm², which was in agreement with data (1. 130 J/cm²) from Joule effect. Therefore, the results of the Joule effect calibration method were reliable and reasonable. The results calibrated by Joule effect were given in Table 1.

Table 1 Determined values of Calorimeter constant and time constant

Temp /K	K /J·cm^{-2}	Δk $\times 10^3$	$\Delta K/K$ (%)	τ /s	$\Delta\tau$	$\Delta\tau/\tau$ (%)
348. 2	1. 1246	4. 0	0. 36	298. 2	1. 8	0. 6
353. 2	1. 1120	2. 7	0. 24	296. 4	2. 5	0. 85
358. 2	1. 1046	5. 5	0. 50	289. 1	2. 0	0. 68
363. 2	1. 0919	6. 6	0. 60	280. 3	2. 3	0. 83
368. 2	1. 0897	5. 9	0. 54	271. 0	3. 1	1. 14
373. 2	1. 0850	4. 4	0. 41	270. 5	4. 0	1. 46

3. 3 *Determination of the Kinetic Parameters*

The experiments were carried out at 75~100 ℃. The initial particle size of gibbsite was 360~400 mesh. In each experiment, a 100± 0. 05 mg sample was dissolved in 5. 00 mL NaOH solution. Calorimetric curve obtained was like Fig. 1. Substituting the values of experimental data in equations (6), (7), the values of $d\alpha/dt$ and α were given. According to equation (11), the reaction-order and apparent constant of reaction rate were obtained from the slope and intercept of plot of $\ln[d\alpha/dt(1-\alpha)^{-\frac{2}{3}}]$ *vs.* $\ln[(R' - \alpha)\cdot(W_0/MV)]$, respectively. The results of a statistical correlation of experimental data using equation (11) were given in Table 2.

4 DISCUSSION

In the degestion reaction of gibbsite, the only reactant in solution was sodium hydroxide. Thus, the reaction rate could be expressed as:

$$v = k \cdot C^{n}_{\mathrm{NaOH}} \tag{15}$$

where n could be calculated from the slope according to equation(11)， it was 1.01. The standard deviation was 0.11. The rate of dissolution of gibbsite could be of first-order. It was independent on the concentration of NaOH solution from 4.19～7.37 mol/L.

Table 2 Kinetic parameters for dissolution of gibbsite

T /K	$-\ln K$	n
348.2	9.732	0.94
353.2	9.032	1.15
358.2	8.667	0.85
363.2	8.435	0.95
368.2	8.142	1.05
373.2	7.783	1.10

The dependence of extraction rate on temperature was tested against the Arrhenius' equation(Fig. 5). The results obey Arrhenius-type relationship $k = k_0 \exp(-E/RT)$.

The activation energy calculated from the slope of the curve in Fig. 5 was 76.85 kJ/mol. The magnitude of the apparent activation energy further evidenced that the reaction was chemically controlled. It was in agreement with that reported by Tatsubiko[1]， Borntrager[9] and Yin Aijun[10].

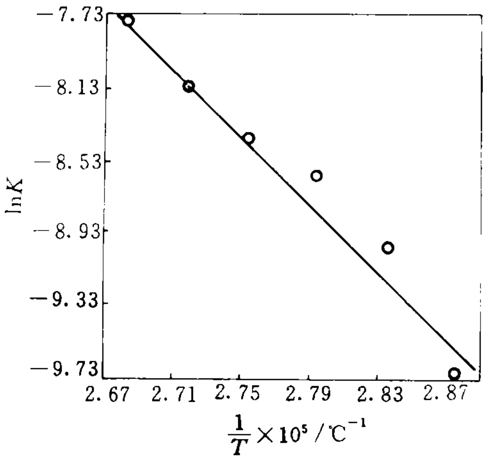

Fig. 5 Effect of temperature on dissolution rate of synthetic gibbsite

The kinetic equation of the dissolution process could be presented as：

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_0 \cdot (R' - \alpha)(1 - \alpha)^{2/3} \cdot \exp(-76\,850/RT) \tag{16}$$

5 CONCLUSIONS

(1) For the dissolution of synthetic gibbsite in NaOH solution， a first-order dependence on the concentration of sodium hydroxide was observed. Apparent activation energy was 76.85 KJ/mol.

(2) The heat conduction-type calorimeter was a very useful tool for obtaining both thermochemical data and kinetic parameters. It was convenient for the investigation of chemical technology and reaction engineering， as well as basic chemistry.

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