

Decomposition of raw materials by mineral acids

Dissolving of raw materials in consequence proceeding chemical reaction is fundamental technological operation of many industrial productions. This process is included in the family of heterogeneous non-catalytic reactions realizing between the solid and liquid phase. One of the important industrial examples is dissolving of phosphates by mineral acids, which represents an initial chemical operation for the fertilizers production. Knowledge of the influence of separate partial steps for different reaction conditions on the reaction rate has a great importance for the designing of industrial reactors. Reaction kinetics of heterogeneous non-catalytic systems deals with this issues. Reaction kinetics use random simplified model ideas for description of the reaction course. These model ideas facilitate the evaluation of fundamental kinetic parameters.

Theoretical fundamentals

Shrinking core model

This model is suitable for description of the reaction course of nonporous solid component with the liquid phase. It is assumed, that the reaction begins currently on whole area of the solid reactant particles and the reactionary interface moves gradually inwards. Two cases can occur. For the first one is assumed, that during the reaction rises porous layer of product or inert containing in raw material, which cleaves on still shrinking core of particles. Size of particles does not almost change during the reaction. For the second case is assumed, that the layer of rising product or inert does not rise on the surface in the consequence of good products solubility or the solid phase detaches from the surface. The shrinking core decreases gradually, until it vanishes finally.

Reaction rate

The stoichiometric equation of irreversible heterogeneous reaction can be generally presented in this form.



where a , b are stoichiometric coefficients.

During the reaction numbers of moles of component A and B change according to stoichiometry. These changes can be set down by the relation (2):

$$\frac{dN_A}{a} = \frac{dN_B}{b}, \quad (2)$$

where N_A and N_B are the actual amount of moles of the components A and B. The reaction rates related to individual initial components according to the stoichiometry equation (1) can be expressed in the form:

$$\frac{r_{AS}}{a} = \frac{r_{BS}}{b}, \quad (3)$$

The reaction rate of the liquid component A on the solid component surface proceeds according to the equation (4):

$$r_{AS} = -\frac{1}{S_B} \cdot \frac{dN_A}{d\tau} = k_s \cdot c_{AS}^n, \quad (4)$$

where r_{AS} is the reaction rate of component A related on outer area unit of the solid component B, k_s is the rate constant, c_{AS} is the concentration of liquid component A on the outer surface of solid component B, S_B is the reaction interface area, τ is time and n is the reaction order with respect to the liquid component A.

The reaction rate of the component A can be described using the equations (2) and (3) in terms of the change of the amount of the component B in the form:

$$r_{AS} = -\frac{1}{S_B} \cdot \frac{a \cdot dN_B}{b \cdot d\tau} \quad (5)$$

For the rate constant in the Eq. (3) can be used the Arrhenius equation for temperature dependence:

$$k_s = A \cdot \exp\left(-\frac{E_A}{RT}\right), \quad (6)$$

where A is the pre-exponential factor, E_A is the apparent activation energy, T is the absolute temperature and R is the general gas constant. Using of substitution of Eq. (6) into the Eq. (4) and after adjustment can be obtained:

$$-\frac{dN_B}{d\tau} = \frac{A \cdot b \cdot S_B \cdot c_{AS}^n}{a} \cdot \exp\left(-\frac{E_A}{RT}\right) \quad (7)$$

The formula for the calculation of the dolomite conversion η_B using the weight of solid phase at the beginning and at a given time is:

$$\eta_B = \frac{m_{B0} - m_B}{m_{B0}} = \frac{N_{B0} - N_B}{N_{B0}}, \quad (8)$$

where m_{B0} is the weight of the solid component B at the beginning of the reaction, m_B is the weight of the solid component B at a given time, N_{B0} is the number of mole of the solid component B on the beginning of the reaction and N_B is the number of mole of the solid component B at a given time. After multiplication of the both sides of the Eq. (8) by N_{B0} and derivation of the formula with respect to time (τ) the relation between N_B and η_B can be derived in form:

$$N_{B0} \frac{d\eta_B}{d\tau} = -\frac{dN_B}{d\tau}, \quad (9)$$

$$S_B = (S_{Bg})_0 \cdot m_{B0} \quad (10)$$

Using of substitution of Eq. (9) into the Eq. (7), using the Eq. (10) and for the reaction conditions where $\eta_B \rightarrow 0$ as $\tau \rightarrow 0$, we can obtain the following equation:

$$\left(\frac{d\eta_B}{d\tau} \right)_{\eta \rightarrow 0} = \left(\frac{b \cdot c_A^n \cdot A \cdot Mr_B \cdot (S_{Bg})_0}{a} \right) \exp\left(-\frac{E_A}{RT} \right) \quad (11)$$

For our purpose is very useful to work with Eq. (11) in the following form:

$$\ln\left(\frac{d\eta_B}{d\tau} \right)_{\eta \rightarrow 0} = \ln\left(\frac{b \cdot c_A^n \cdot A \cdot Mr_B \cdot (S_{Bg})_0}{a} \right) - \frac{E_A}{RT}, \quad (12)$$

which expresses the dependence of the $\ln(d\eta_B/d\tau)_{\eta \rightarrow 0}$ on the reciprocal values of the reaction temperature $1/T$. From the experimental data and using the Eq. (12) it is possible to evaluate the values of the apparent activation energy E_A using the method of least squares.

In this case is very convenient to relate all used quantities to the start of the reaction, because at this point all the information and data about the reaction system are available.

Device description

All experiments take place in a batch isothermal stirred reactor. The Reactor consists of a glass beaker with volume 800 cm^3 placed in the circulatory thermostat (Julabo MA-12), which maintains the constant temperature during the whole measurement. The reaction

temperature in the reactor is watched by the mercury thermometer. Stirring of the reactive mixture is provided by an axially placed metal stirrer with four paddles, which is powered by the electric engine with adjustable rotation speed. The inclination of the paddles is 45° and it is placed in the third of height of stirring volume. The reaction time is watched by a stop-watch, the sample weight before and at the end of the reaction is measured by weighing on an electronic balance (available are Mettler AE 2000).

Work instruction

1. Preparation of 2 dm^3 1% nitric acid by dilution of calculated amounts of concentrated HNO_3 (65 % weight) by distill water.
2. Measuring of dependence of conversion degree on time.

The reactor containing 500 cm^3 nitric acid of known concentration is placed into the thermostat. After the temperature in the reactor will reach and maintain at the demanded value, one gram of phosphate particles of the defined size is put into the reactor. This moment is taken as beginning of the reaction. Weighing is carried on with an accuracy 0.0001 g. The reaction time is watched by a stop-watch. Stopping of the reaction in advance of chosen moment is practiced by stopping the stirrer, removing the reactor from the thermostat, sedimentation of the particles on the bottom of the reactor, flowing out of liquid state and dilution residual reactionary mixture by cooled distill water. This moment is taken as the end of the reaction. The decantation by distill water is repeated twice. Five-minutes stirring of the sample in distill water succeeds to after the sufficient dilution of the residual acid. This is necessary for the washing out the last acid residuals from pores of the partial reacted sample. Next step is separation of the unreacted part of sample from liquid phase on a glass frit. Sample drying to constant weight proceeds in laboratory drying box at temperature around $130 \text{ }^\circ\text{C}$ for 1,5 h. The weight of the cold frit with the rest of the sample is determined in the end.

Reaction conditions:

The concentration of the nitric acid: 1% hm. HNO_3

The reaction temperatures: $T_1 = 30 \text{ }^\circ\text{C}$ a $T_2 = 40 \text{ }^\circ\text{C}$

Reaction times: for $T_1 = 30 \text{ }^\circ\text{C} \Rightarrow 180 \text{ s}, 350 \text{ s}, 500 \text{ s}, 750 \text{ s}, 920 \text{ s}$

For $T_2 = 40 \text{ }^\circ\text{C} \Rightarrow 180 \text{ s}, 350 \text{ s}, 500 \text{ s}, 600 \text{ s}, 750 \text{ s}$

A solid phase: apatit Kola super ($[3\text{Ca}_3(\text{PO}_4)_2]\cdot\text{CaF}_2$), fraction 0,315 – 0,400 mm

Experimental data processing

Goal of this work is to obtain dependence of the conversion degree of the phosphate in the phosphoric acid on time for two temperatures.

The parameters of the dependence $\eta_B = f(\tau)$, which has almost a linear course for the initial stage of decomposition and passes through zero, can be evaluated from the experimental data with utilizing of linear regression. Derivation of the linear function offers

the quantity $\left(\frac{d\eta_B}{d\tau}\right)_{\eta \rightarrow 0}$, which is almost proportional to the reaction rate in its beginning. The

apparent activation energy can be evaluated by means of linear regression using the Eq. (12) for the dependence of the logarithmic value of the change of the conversion degree with time on the reciprocal values of the reaction temperature $1/T - \ln(d\eta_B/d\tau) = f(1/T)$.

List of symbols:

- a stoichiometric coefficient of the component A
- b stoichiometric coefficient of the component B
- A pre-exponential factor ($\text{mol}^{1-n} \text{m}^{3n-2} \text{s}^{-1}$)
- c_A concentration of the liquid component A in the bulk phase (mol m^{-3})
- c_{AS} concentration of the liquid component A on the surface of the solid component B (mol m^{-3})
- d derivative (-)
- E_A apparent activation energy (J mol^{-1})
- k_S reaction rate constant related on the outer area of solid component B ($\text{mol}^{1-n} \text{m}^{3n-2} \text{s}^{-1}$)
- m_B weight of the solid component B in time τ (g)
- m_{B0} weight of the solid component B at the beginning of the reaction (g)
- M_{rB} molar weight of the solid component B (g mol^{-1})
- n reaction order with respect to the liquid component A (-)
- N_A actual amount of moles of the component A (mol)
- N_{B0} amount of moles of the component B at the beginning of the reaction (mol)
- N_B actual amount of moles of the component B (mol)

- r_{AS}, r_{AB} reaction rate of the component A related on the reaction interface of the solid particles ($\text{mol m}^{-2} \text{s}^{-1}$)
- S_B reaction interface area (m^2)
- $(S_{Bg})_0$ reaction interface area related to the weight of the solid component ($\text{m}^2 \text{g}^{-1}$)
- T temperature (K)
- η_B conversion degree of the solid component B (-)
- τ time (s)

Content of the final report:

- **Short** theoretical introduction including **the reaction equation** and a **short** description of the experimental section (the calculation of the acid dilution)
- Tables with experimental data
- Graphical dependence - $\eta_B = f(\tau)$ and $\ln(d\eta_B/d\tau) = f(1/T)$
- The apparent activation energy E_A evaluation

Use MS Word and MS Excel for the processing of the experimental data and the final report.