

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 family of heterogeneous uncatalysed reactions realizing between solid and liquid phase. One of important industrial examples is dissolving of phosphates by mineral acids, which represents initial chemical operation for fertilizers production. Knowledge of influence of separate partial steps for different reaction conditions on reaction rate has a great importance for designing of industrial reactors. Reaction kinetics of heterogeneous uncatalysed systems deals with this problems. Reaction kinetics uses simplified model ideas to description of reaction course. Model ideas facilitate to evaluate fundamental kinetic parameters of existing system.

Theoretical fundamentals

Shrinking core model

This model is suitable for description of reaction course of nonporous solid component with liquid. It is assumed, that reaction begins currently on whole area of solid reactant particles and 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 change almost during the reaction. For the second case is assumed, that layer of rising product or inert does not rise on surface in consequence of good products solubility or solid state detaches from the surface. Shrinking core decreases gradually, untill it vanishes finally.

Reaction rate

Stoichiometric equation of irreversible heterogeneous reaction can be generally formulated in this form.



where a , b are stoichiometric coefficients.

Numbers of moles of component A and B change during the reaction according to stoichiometry. These changes can be written by relation.

$$\frac{dN_A}{a} = \frac{dN_B}{b}$$

where N_A and N_B are actual amount of moles of component A and B. Between reaction rates related to individual initial components passes for this following relation with respect to stoichiometry (1)

$$\frac{r_{AS}}{a} = \frac{r_{BS}}{b}$$

Depletion rate of liquid component A on the solid component surface proceeds according to equation.

$$r_{AS} = -\frac{1}{S_B} \cdot \frac{dN_A}{d\tau} = k_S \cdot c_{AS}^n \left(= -\frac{1}{S_B} \cdot \frac{a \cdot dN_B}{b \cdot d\tau} \right),$$

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

Shrinking core model for initial reaction stage offers following relation. This relation is accepted only under these conditions – chemical reaction is control process, system is isothermal and acid concentration does not change during the reaction:

$$\left(\frac{d\eta_B}{d\tau} \right)_{\eta_B \rightarrow 0} = \frac{3 \cdot b \cdot k_S}{a \cdot \delta_B \cdot R_0} \cdot c_{AS}^n, \quad (2)$$

where R_0 is initial particle radius, δ_B is molar density of component B a η_B is conversion degree of solid component B.

For deduce of explicit relation were used following equations:

$$N_B = \frac{m_B}{M_B} = \frac{\rho_B \cdot V_B}{M_B} = \frac{\rho_B \cdot \frac{4}{3} \pi R^3}{M_B}, \quad \eta_B = \frac{m_{B0} - m_{B\tau}}{m_{B0}} = \frac{\frac{4}{3} \pi R_0^3 - \frac{4}{3} \pi r^3}{\frac{4}{3} \pi R_0^3}$$

where M_B is molar weight of component B, m_B is weight of component B, ρ_B is density of solid component B, V_B is volume of solid component B, m_{B0} is weight of solid component B at the beginning of the reaction, $m_{B\tau}$ is weight of solid component B in any time τ .

Above explicit relation (2) can be linearized by logarithmic operation in form:

$$\ln \left(\frac{d\eta_B}{d\tau} \right)_{\eta_B \rightarrow 0} = \ln \frac{3 \cdot b \cdot k_S}{a \cdot \delta_B \cdot R_0} + n \cdot \ln c_{AS} \quad (3)$$

and we can evaluate reaction order n by solution of equation system for different acid concentration.

Device description

All experiments are proceeded in a batch isothermal stirred reactor. Reactor consists of a glass 800 cm³ beaker placed in thermostat (type U-10 provided by thermoregulator Vertex), which enables constant temperature during measurement. Temperature in reactor is watched by mercury thermometer. Stirring of reactionary mixture is provided by an axially placed glass two-vaned stirrer, which is powered by elektromotor with adjustable rotation speed. Inclination of vanes is 45° and its placing is from bottom in the third of height of stirring volume. Reaction time is watched by stop-watch, 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 5 dm³ 10% and 1% orthophosphoric acid by dilution of calculated amounts of concentrated H₃PO₄ (86 % weight) by distill water.
2. Measuring of dependence of conversion degree on time.

Reactor containing 500 cm³ orthophosphoric acid of known concentration is placed into the thermostat. After achievement of constant temperature is put sample into the reactor approximately of one gramme phosphate particles, which have defined size. This moment is taken as beginning of the reaction. Weighing is practised with accuracy 0.0001 g. Reaction time is watched by stop-watch. Stopping of the reaction in advance of chosen moment is practised by stopping the stirrer, removal of reactor from the thermostat, sedimentation particles on the bottom of the reactor, flowing out of liquid state and dilution residual reactionary mixture by cool distill water. This moment is taken as reaction time. Decantation by distill water is practised yet twice. Five-minute stirring of sample in distill water succeeds to after sufficient dilution of residual acid. This is necessary for washing out the last acid residuals from pores of partial reacted sample. Next step is separation of unreacted part of sample from liquid phase with a glass frit. Sample drying to constant weight proceeds in laboratory drying box at temperature cca 130°C for time cca 1,5 h. Weight of cool frit with residual of sample is determined in the end.

Reaction conditions:

temperature T = 30°C

reaction time: for 10% H₃PO₄ ⇒ 200 s, 420 s, 600 s, 750 s, 920 s

for 1% H₃PO₄ ⇒ 400 s, 600 s, 700 s, 800 s, 1000 s
solid state: apatit Kola super ([3Ca₃(PO₄)₂].CaF₂), fraction 0,200 – 0,250 mm

Experimental data working

Goal of this work is to obtain dependence of conversion degree of phosphate on time for two concentrations of orthophosphoric acid. Conversion degree value is calculated by means of this relation:

$$\eta_B = (m_{B0} - m_{B\tau}) / m_{B0},$$

where m_{B0} is initial weight of phosphate and $m_{B\tau}$ is weight of reacted phosphate.

Parametres of 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 linear function offers quantity $\frac{d\eta_B}{d\tau}$, which is almost proportional to reaction rate in its beginning. For reaction order determination is used equation (3). Reaction order can be evaluated by means of linear regression of dependence of logarithm of change of conversion degree with time on logarithm of orthophosphoric acid concentration - $\ln(d\eta_B/d\tau) = f(\ln c_A)$.

List of symbols:

- a.....stoichiometric coefficient of component A
- b.....stoichiometric coefficient of component B
- c_{AS} concentration of liquid component A on outer surface of solid component B
[mol.m⁻³]
- k_S reaction velocity constant related on outer area unit of solid component
B [mol.¹⁻ⁿ.m³ⁿ⁻².s⁻¹]
- m_B weight of solid component B [kg]
- m_{B0} weight of solid component B at the beginning of the reaction [g]
- $m_{B\tau}$weight of solid component B at any τ [g]
- M_B molar weight of solid component B [kg.mol⁻¹]
- n reaction order with respect to liquid component A
- N_A actual amount of moles of component A [mol]
- N_B actual amount of moles of component B [mol]

r_{AS} reaction rate of component A related on reactionary interface [$\text{mol.m}^{-2}.\text{s}^{-1}$]
 R_0 initial radius of solid particle [m]
 S_B reaction interface area [m^2]
 V_B volume of solid component B [m^3]
 δ_B molar density of solid component B [mol.m^{-3}]
 η_B conversion degree of solid component B [-]
 ρ_B density of solid component B [kg.m^{-3}]
 τ time [s]

Content of protocol:

- Short theoretical introduction including reaction equations and description of experimental section
- Measuring data table
- Graphical dependence ($\eta_B = f(\tau)$, $\ln(d\eta_B/d\tau) = f(\ln c_A)$)
- Reaction order evaluation

Use MS Word and MS Excel to interpretation of measuring data.