

Lesson 8

The simplest concept of chemical kinetics

Chemical kinetics is the science on the chemical conversion rates. It is no possible to study the reaction mechanisms and the models construction of technology processes including the chemical stages. We confine oneself to acquaintance with the simplest notions and the simplest examples.

Chemical reaction intensity is expressed usually by **the reaction rate** W , that is by the substance quantity reacting during time in given system. We understand under substance quantity the component mol number or any connecting with that value. Then

$$W = -\frac{dn}{dt}.$$

Under specific reaction rate one's understand the substance quantity reacting during unit time in the unit of reaction space:

$$W_V = -\frac{1}{V} \frac{dn}{dt} -$$

for the reactions proceeding in the volume V (**homogeneous reactions**), and

$$W_S = -\frac{1}{S} \frac{dn}{dt} -$$

for the reactions going on the surface S (**heterogeneous reactions**).

If the same reactions occur in the volume and on the surface, then its rate follows from the equation

$$-\frac{dn}{dt} = W_S S + W_V V.$$

Primary data of kinetic experiments are the set of chemical component concentrations or some proportional to them values for various reaction times. Using these data ones can construct the kinetic curves «concentration – time».

Then the reaction rate for given time is determined as tangent of angle of slope of the kinetic curves obtained experimentally.

The equation for the reaction rate can be presented in the form

$$\varphi = k[A]^\alpha [B]^\beta \dots \quad (1)$$

where $\alpha, \beta \dots$ are the partial reaction orders relatively to the components A, B, \dots , and $[A], [B]$ are the concentrations of these components КОМПОНЕНТОВ.

As a rule, the reactions include several elementary stages.

Elementary reactions are related to the reactions of zero, first, second order. The most of chemical reactions can be presented as the some combinations of some elementary stages.

Usually ones extract following simple combinations: parallel (competitive, simultaneous); consecutive; reversible reactions. There are complex reactions combined two or three called types. The equation (1) received on the base of experimental data or on the base of formal kinetics theory have a physical sense, when the reaction orders are prime positive numbers. The fractional orders can be called apparent.

Let consider simple examples of simple reaction scheme for volume reactions.

In the case of **simple reaction of first order**



its rate is proportional to the concentration A :

$$d[A]/dt = -k[A]. \quad (3)$$

The analogous equation is correct for the reaction product

$$d[B]/dt = -k[B].$$

Due to the substance conservation, we have

$$[A] + [B] = [A]_0 + [B]_0 = \text{const},$$

and only one equation (3) is enough.

Integration gives

$$[A] = [A]_0 \exp(-kt), \quad (4)$$

where $[A]_0$ is initial concentration A . That is the reagent consumption during time goes exponentially (fig.1).

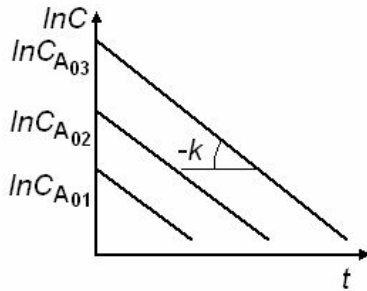


Fig. 1

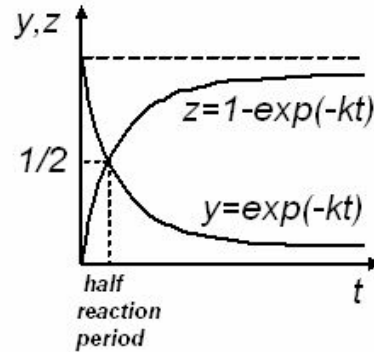


Fig. 2

Angle of inclination of straight line $\ln[A]$ determines the reaction rate constant. The value

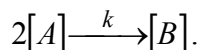
$$t_{1/2} = \frac{\ln 2}{k}$$

is half reaction period (Fig.2). The relative concentration are used on this figure:

$$y = \frac{[A]}{[A]_0 + [B]_0}, \quad z = \frac{[B]}{[A]_0 + [B]_0}, \quad y + z = 1.$$

Rate constant for the reaction of first order is measured in 1/s.

The simple reaction of second order can be written as



In this case the equation for the rate has the form

$$d[A]/dt = -2k[A]^2. \quad (5)$$

We shall find after integration

$$[A] = \frac{[A]_0}{1 + 2kt[A]_0}. \quad (6)$$

The dependence of inverse concentration on time is straight line with the inclination $2k$ (Fig.3). For various initial concentrations, we have the set of straight lines. The reaction rate constant is measured in

$1/(\text{concentration dimension} \cdot \text{s})$

in this case.

We can obtain from experimental data

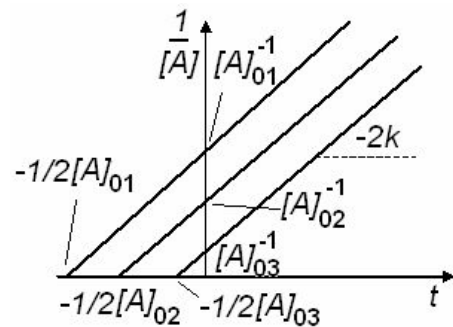
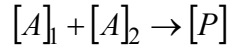


Fig. 3

$$k = \frac{[A]_0 - [A]}{2[A]_0[A]t} \text{ and } t_{1/2} = \frac{1}{2k[A]_0}.$$

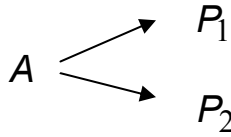
Unlike the first order reaction, half reaction period depends on reagent initial concentration.

The reaction



can be other example, where two molecules participate in the product formation.

When we study two parallel reactions of first order with the rates k_1 and k_2 , reaction scheme takes the form



Only two equations are independent from differential equations for the reagent and for products

$$\begin{aligned} d[A]/dt &= -(k_1 + k_2)[A], \\ d[P_1]/dt &= k_1[A], \\ d[P_2]/dt &= k_2[A]. \end{aligned} \quad (7)$$

The integration gives

$$[A] = [A]_0 \exp(-(k_1 + k_2)t). \quad (8)$$

$$[P_1] = \frac{k_1}{k_1 + k_2} [A]_0 [1 - \exp(-(k_1 + k_2)t)], \quad (9)$$

$$[P_2] = \frac{k_2}{k_1 + k_2} [A]_0 [1 - \exp(-(k_1 + k_2)t)]. \quad (10)$$

Concentrations change in time is shown for this case on the Fig.4.

The reagent consumption and product generation obey to the rate law of first order. The graphs of $\ln[A]$, $\ln([P]_{1\infty} - [P]_1)$, $\ln([P]_{2\infty} - [P]_2)$ on time are straight lines with the inclination tangent $-(k_1 + k_2)$.

To determine the reaction constants from experiment, it is necessary to exclude from (9), (10) the item in square brackets with the help of (8). As a result, we shall find

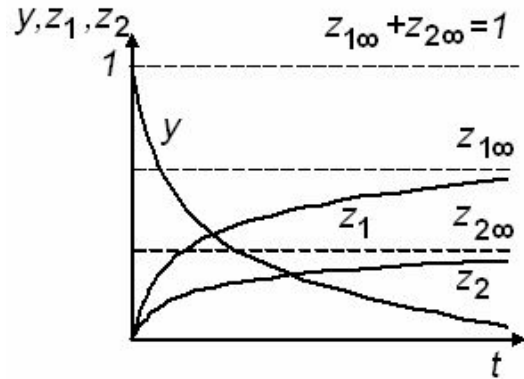


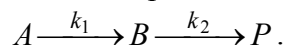
Fig. 4

$$\frac{[P]_1}{([A]_0 - [A])} = \frac{k_1}{k_1 + k_2} \quad (11)$$

and

$$\frac{[P]_2}{([A]_0 - [A])} = \frac{k_2}{k_1 + k_2}. \quad (12)$$

The sequence of two reactions corresponds to the scheme



It is necessary to distinguish two variants.

When $k_1 \gg k_2$, intermediate product is few reactive in comprising with the reagent. The first stage accomplishes practically before second stage start. As a result, one can study each stage separately as the reaction of first order.

When $k_1 \ll k_2$, second stage follows for the first one very quickly, hence it is right for any time

$$[B] \ll [A] \text{ and } [P].$$

We can assume at the mathematical model formulation. $d[B]/dt \approx 0$. Thus approach is called the **method of quasi stationary concentrations of Bodenshtain**.

In general case we come to differential equations

$$\begin{aligned} d[A]/dt &= -k_1[A], \\ d[B]/dt &= k_1[A] - k_2[B], \\ d[P]/dt &= k_2[B], \end{aligned} \quad (13)$$

that is integrated analogous to previous ones.

Catalytic reactions, when the catalyst participates in the reaction no changing its stoichiometry, forms the large group of the reactions. If the intermediate product plays the role of catalyst, we speak on **autocatalytic reaction**.

The reaction scheme is formal description of the reaction. It is macroscopic reaction appearance.

The reaction rate depends on the conditions of its implementation: temperature, pressure, external field's presence.

There are several equations applicable to description of the temperature dependence of the reaction. **The Arrhenius law** is the best-known from them

$$k = k_0 e^{E_a/RT}. \quad (14)$$

where k_0 is preexponential factor, E_a is activation energy.

The large significance for the reaction belongs to the **activation volume**. Particularly, this value determines the dependence of the reaction rate on the pressure.

The kinetics of **heterogeneous reaction** is more complex and is discussed in the literature together with the surface properties.

The solid phase reactions have a features which are discussed during the lectures by specially way.

The basic features consist in the following: 1. the reaction localization in the interface; 2. specific role of the transfer process due to the small mobility of the reagent or/and products; 3. the presence of complex feedbacks connections between the physical and chemical phenomena of various natures. Theory of **topochemical reactions** is the basis for solid phase processes description.

The material synthesis and surface modification, coating synthesis on the substrate are the examples of the models of high temperature technology processes with the chemical reactions. These examples are analyzed in 8 and 9 lectures.

Diffusion

The diffusion plays the significant role, when the reaction proceeds in heterogeneous system. Chemical reaction can be localized in one or several phases.

Correspondingly, the different problems of diffusion kinetics appear. The features of them depend on the diffusion mechanisms in phases.

The most quickly diffusion happens in gases. In the liquids, the diffusion goes more slowly, where the particles act with other particles. The most slowly diffusion rate is observed in solid phase, where several diffusion mechanisms can be distinguished.

In whole, the diffusion physics is large part of solid physics. The theory is based on the fundamental conception of physical kinetics and irreversible thermodynamics.

The most general diffusion law connects with name Fick (Fick law) established it experimentally

$$\mathbf{J} = -\rho D \text{grad } C. \quad (15)$$

It is follows from (15), that the mass flux is proportional to concentration gradient. Diffusion flux is determined by the relation

$$\mathbf{j} = -D \text{grad } C.$$

The first value is measured in kg/(m²s) or in g/(cm²s); second – in cm/s.

Here C is mass concentration of component; and D is diffusion coefficient, m²/s или cm²/s.

Diffusion coefficient depend on the temperature correspondingly to Arrhenius law

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right).$$

Fick law is similar to Fourier law^ the diffusion and thermal conduction processes are similar in the firs approximation. The differential equation that is necessary to describe the diffusion process is similar to thermal conduction equation also. So, for no moving medium, we have

$$\rho \frac{\partial C}{\partial t} = \text{div} (D\rho \text{grad } T) + \sigma',$$

where σ' is the sum of sources and sinks in chemical reactions.

If the substance density is constant, we shall find

$$\frac{\partial C}{\partial t} = \text{div} (D \text{grad } T) + \sigma, \quad \sigma = \frac{\sigma'}{\rho},$$

or for Cartesian coordinate system -

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) + \sigma.$$

One dimensional diffusion equation have a form

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + \sigma.$$

The temperature diffusivity is analogy for diffusion coefficient in thermal conduction theory

$$a = \frac{\lambda}{c\rho}.$$

It is typically for gases in usual conditions

$$Le = \frac{D}{a} \sim 1.$$

For solid bodies $Le \ll 1$. This value is called **Lewis number**.

The special similarity numbers have a significant role at the diffusion processes description. **Sherwood number** or diffusion Nusselt number

$$Sh \equiv Nu_D = \frac{\beta d}{D},$$

where d is specific linear size, β is mass emission coefficient is the relation

$$\mathbf{j} = \beta \Delta C,$$

analogous to Newton-Richman law; ΔC is concentration difference; **Shmidt criterion** (the analogy for Prandl number)

$$Sc = \frac{v}{D} -$$

between them.

Besides the law (15), the generalized Fick law has a significant role in the diffusion theory

$$\mathbf{j}_i = - \sum_{j=1}^{n-1} D_{ij} \text{grad } T_j, \quad i=1,2,\dots,n, \quad (16)$$

where n is component number for multi component system. Only $n-1$ component are independent between them. D_{ij} are partial diffusion coefficients.

The more complex mass transfer mechanisms are known.

Examples of diffusion problems are studied during the lection.