BUILDING CHEMISTRY

LAB 4

REACTION KINETICS

THEORETICAL BACKGROUND

The aim of the study of chemical kinetics is to evaluate the rate and the mechanism of a chemical reaction. The reaction rate describes the speed at which the changes in concentration of the chemical reagents occur, whereas the reaction mechanism describes the subsequent stages of the total reaction. The reaction rate is of great theoretical and practical importance. Based on the reaction rate, it is possible to calculate the efficiency of the process in industrial conditions.

From reaction kinetics' point of view, following types of reactions can be distinguished: homogeneous (occurs within one gas or liquid phase) and heterogeneous (occurs at the border of two phases). In building materials, the rate of the chemical processes can be considerably diverse. Gypsum hydration and setting takes up to a few minutes, whereas the hardening and setting processes of cement take days, or even years.

The most important factors that can influence the reaction rate are: reagents' properties, reagents' concentration, temperature and catalysts. Chemical reaction is a process where one chemical compound (substrate) transforms into another chemical compound (product). Those reactions are contractually described with the use of chemical equations. In reality, chemical equations do not describe all of the chemical reaction's stages that occur in a series of steps. The complete sequence of those steps is called a reaction mechanism.

Reaction rate (v) describes the course of a chemical reaction in a quantitative way.

$$v = \frac{1}{V} \cdot \frac{dn}{dt}$$

Where: n – number of moles of a reagent

V – volume of the solution

t – time

The equation describes the change in the number of moles of a reagent in time, with respect to the volume of the reacting system. The isochoric process (V=const) occurs as per the following equation:

$$\mathbf{nA + mB \rightarrow lC + zD}$$

therefore, the reaction rate equation can be transformed into:

$$v = \frac{d\left(\frac{n}{V}\right)}{dt} = \frac{dc}{dt}$$

$$v = \frac{dc_p}{dt}$$

$$v = -\frac{dc_s}{dt}$$

where: c - concentration

c_p – concentration of the product,

c_s – concentration of the substrate.

In order to define the reaction rate in t', the relationship f=c(t) must be determined, e.g. with the use of the kinetic curve, and then by the determining the derivative dc/dt in time t', which in definition is equal to the tangent α to the kinetic curve at the t' point (fig. 1). If the determination of the reagent's concertation is not possible, the kinetic curve can present the relationship between the reaction time and other properties of the chemical system, e.g. pressure, viscosity, etc.

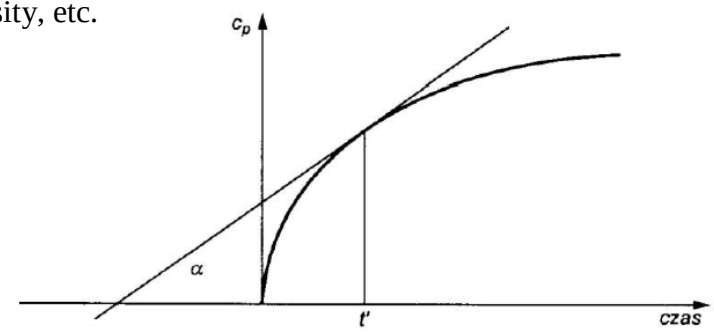

Fig. 1. Kinetic curve

With the two values of the substrate concentration - c_1 in t_1 and c_2 and t_2, it is possible, based on concentration difference $\Delta c = c_2 - c_1$, to determine the average value of the reaction rate (v_s) in $\Delta t = t_2 - t_1$ interval, where $v_s = \Delta c/\Delta t$.

Relationship between reaction rate and substance concentration

In order for a chemical reaction to occur, the molecules must meet the following conditions:

- collide with each other;
- carry enough energy for the collision to be effective, i.e. the amount of energy that is at least equal to the amount of the activation energy,
- collide with proper orientation - be properly oriented towards each other at the time of collision

The reaction rate depends on the number of the effective collisions between the reacting molecules. In a given volume, the amount of those collisions is proportional to the substrate concentration. The relationship between the reaction rate and the reagents' concentration is described by the kinetic equation of the chemical reaction:

$$v = k \cdot c_A^n \cdot c_B^m$$

where: c_A – concertation of the substrate A,

c_B – concentration of substrate B,

k – reaction rate constant,

n – the order of reaction for component A,

m - the order of reaction for component B.

For a one-step reaction, n and m factors are equal to the stoichiometric factors of the proper chemical equation. For complex reactions, the rate equation is only an approximate equation and the reaction ratio depends on the slowest stage of the reaction. Reaction rate constant k is equal to the reaction rate when the concentrations of the reagents are equal, and it is a function of temperature.

Relationship between reaction rate and temperature

The minimum amount of energy that molecules must carry in order for the collision to be effective is called activation energy (E), and the molecules that carry the amount of energy equal to or higher than the activation energy are called active molecules. The raise of temperature causes increase not only in the amount of the active molecules, but also in the number of the effective collisions, therefore it speeds up the reaction rate.

The relationship between temperature and the reaction rate is described by the Arrhenius equation:

$$k = Ae^{-\frac{E}{RT}}$$

where: T – temperature [K],

R – universal gas constant,

E – activation energy,

A – pre-exponential constant or frequency factor, depending on the temperature and the frequency of molecule collisions when all concentrations are 1 mol/L, and on whether the molecules are properly oriented when they collide.

Relationship between chemical reaction and the presence of catalysts

Catalysts are the substances that change the reaction rate and after the reaction's completion remain unchanged. Catalysts provide an alternative reaction mechanism by lowering the reaction activation energy. They do not change the stoichiometric equation or the chemical reaction balance, they only accelerate the achievement of this stage.

Two types of catalysts can be distinguished: positive catalysts (accelerate the reaction) and negative catalysts (delay the reaction), called inhibitors.

Reaction rate in heterogeneous systems

In heterogeneous systems, e.g. solid-liquid or solid-solid (such systems are most often the main point of interest in building chemistry), chemical reactions occur at the interface between phases. In such systems, the transport of the matter (diffusion) is of particular importance. The diffusion process or small contact surface between the substrates can constitute a significant limitation, e.g.:

- removal of products from the reaction place and provision of a new portion of the substrate in that place,
- spillover of the reagents into another layer of product.

Mixing, as well as the raise of temperature, cause the increase in the diffusion rate, and therefore also in the reaction rate. Diffusion plays a crucial role not only in the multiphase systems, but also in the single-phase systems.

PRACTICAL SESSION

EFFECT OF CONCENTRATION OF SUBSTRATES ON REACTION KINETICS

Equipment: 4 polypropylene beaker (50 ml), pipette, wash bottle, magnetic stirrer, stopwatch
Reagents: distilled water, HCl (2 mol/dm^3), $Na_2S_2O_3$ (1 mol/dm^3)

PROCEDURE

1. Place 50 cm^3 of distilled water and 2 cm^3 of HCl into each beaker.
2. Add 2 cm^3 of sodium thiosulfate to the first beaker and determine (using the stopwatch) the time elapsed from the moment of the sodium thiosulfate addition until the moment of the first turbidity appearance.
3. Place 4, 6 and 10 cm^3 of sodium thiosulfate in the next three beakers and determine (using the stopwatch) the time elapsed from the moment of sodium thiosulfate addition until the moment of the first turbidity appearance.
4. The turbidity of the solution is the effect of precipitation of the colloidal sulfur in accordance with the chemical equation:

$$Na_2S_2O_3 + 2\,HCl \rightarrow 2\,NaCl + SO_2 + S\downarrow + H_2O$$

5. Assuming that the solution's opacity results from always having the level of sulfur concentration unchanged, the reaction rate can be considered inversely proportionate to the time that elapsed until the first turbidity appeared.

$$v = \frac{c_s}{t}$$

where: c_s – sulfur concentration, t – time;
hence:

$$v = const(1/t)$$

Based on this formula, it is possible to calculate a relative reaction rate (v_n')

$$v_1 = const\left(\frac{1}{t_1}\right) \quad v_1' = 1$$

$$v_2 = const\left(\frac{1}{t_2}\right) \quad v_2' = \frac{v_2}{v_1} = \frac{t_1}{t_2}$$

$$v_3 = const\left(\frac{1}{t_3}\right) \quad v_3' = \frac{v_3}{v_1} = \frac{t_1}{t_3}$$