Basic and Advanced Calculations for the Solution of Problems in the Chemical Industry

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CHAPTER 1

INTRODUCTION

Organization of processes in the chemical industry

Chemical technology encompasses knowledge about production processes carried out in the chemical industry and in other branches where chemical methods are used. In the course of production processes, a number of activities are performed (called unit operations), in which processed materials undergo chemical or physical changes. In the chemical industry, an apparatus set, called an installation, includes reactors and other devices used for the control of the production process, for transfer of materials and energy, for storage and transport of raw materials and products, for treatment and disposal of wastewater and post-production gases discharged from the installation. Chemical technology includes the methods of processes organization, which depend on the properties of processed materials and on the mechanism of their transformation.

Industrial installations are in active contact with their surroundings. Raw materials and energy are supplied from outside, whereas products and production wastes are removed. Energy streams are also directed out of the facility, e.g. heat contained in the product, in water vapour, which is a by-product of the process, as well as in water, which cools the apparatus. The kind and intensity of material and energy streams that are introduced and discharged from the installation are the basic data characterizing its activity, the material efficiency, the energy consumption, the amount and type of wastes and the amount of pollutant emissions.

Organization of the technological process includes the structure of the production equipment, as well as the kind of activities necessary for the proper realization of the production program, including the assortment, quantity and quality of the products. The principles of technological process organization applied in the chemical industry, are the basis for chemical technology.

Three levels of the process organization can be distinguished in chemical plants. The first applies to a single apparatus: reactor, mass or heat exchanger etc., which can be used for a batch process or for a continuous one. In flow through apparatus, the material streams may be transported in a co-current, counter-current or other arrangement. Heat can be transferred through a barrier separating two different materials, or directly, when they are in contact with each other, e.g. when heating solid materials with hot gases.

The second level applies to a technological installation usually consisting of several objects: reactors, heat or mass exchangers and many other. In these systems, several devices may be connected in parallel, or in a series called a cascade. A specific solution, often used in chemical plants, is a recycle loop, a complex system where a part of the stream, leaving one of the apparatus, is directed to it again (Fig.1.1).

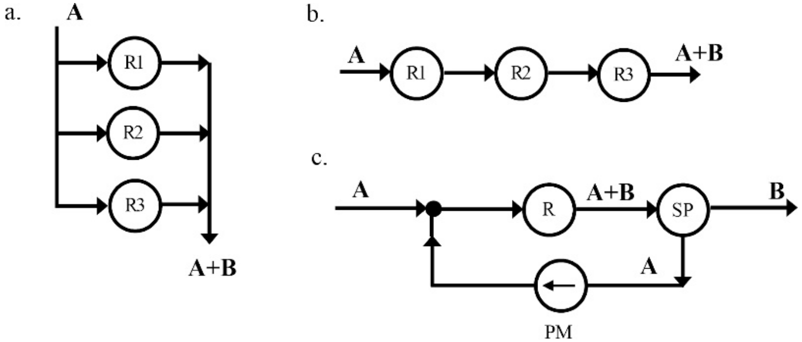

Fig. 1.1. Reactor systems: a) parallel, b) in series, c) recycle stream, R – reactor, SP – separator, PM – circulation pump.

The third level of the process organization relates to the entire plant (or its separate independent part) consisting of a number of different installations. The appropriate organization of this complex system should ensure an effective interaction of individual installations, rational management of raw materials and energy, appropriate level of process safety, as well as an effective protection of the environment from chemical contamination and other undesirable effects.

CHAPTER 2

CHARACTERISTICS OF CHEMICAL PROCESSES

The term "chemical reaction" used in this book refers only to the transformation of a substrate into a product, whereas the term "chemical process" includes, in addition to the reaction, the accompanying phenomena of mass, energy or electrical charge transfer. A full description of the chemical process includes the conditions under which the process takes place, its progress and kinetics, as well as the final result.

The parameters that determine the process conditions are temperature, pressure, reagent concentrations, mass flow, energy flow, etc.

The measure of progress in a chemical reaction is the conversion, which indicates how much of the substrate has been processed into the product;

The kinetics of the process are represented by the rate of chemical and physical transformations taking place in reactors or other apparatus;

The result of the process is characterized by its productivity (the amount of product produced per unit of time), as well as material efficiency, energy efficiency, etc.

2.1. State of reagent system

A system of components which can undergo chemical transformations can be in one of the following states:

- the state of thermodynamic equilibrium, which is also a state of chemical equilibrium, in which the composition of the reagent mixture does not change;
- the state of reaction, in which the composition of the system changes due to chemical transformations;
- the inhibition state of chemical reactions, in which equilibrium has not been attained, but the reactions do not proceed, e.g. due to low temperature.

2.2. Conversion and material yield

To measure the progress in a chemical process, the conversion of substrate is usually used, which indicates how much of the initial amount of the substrate has been processed into the product. If the reaction 1A = 1B is carried out in a closed tank reactor, the conversion of substrate A to product B, i.e. $x_{(A\to B)}$, is determined as follows:

$$x_{(A\to B)} = \frac{n_0[A] - n[A]}{n_0[A]} \tag{1}$$

$$\text{or } x_{(A\to B)} = \frac{m_0[A] - m[A]}{m_0[A]} \tag{2}$$

$n_0[A]$, $m_0[A]$ - initial number of moles or initial mass of substrate A
$n[A]$, $m[A]$ - number of moles or mass of substrate A that remained unprocessed in the course of the reaction.

The result of the completed process may be described by the material efficiency, η, of the transformation of substrate A into product B (expressed in molar or mass units):

$$\eta = \frac{n_0[A] - n_k[A]}{n_0[A]} \tag{3}$$

$$\eta = \frac{m_0[A] - m_k[A]}{m_0[A]} \tag{4}$$

$n_k[A]$, $m_k[A]$ - number of moles or mass of substrate A at the end of the process.

In a process carried out in a flow through reactor operating under steady state conditions, the final conversion $x_{(A\to B)}$ may be determined taking into account the stream of substrate A fed to the reactor and the stream of the unreacted substrate A discharged from it:

$$x_{(A\to B)k} = \frac{W_E[A] - W_Y[A]}{W_E[A]} \tag{5}$$

$$\text{or } x_{(A\to B)k} = \frac{G_E[A] - G_Y[A]}{G_E[A]} \tag{6}$$

$W_E[A]$ and $W_Y[A]$ denote the flow rate of substrate A going into and out of the reactor, respectively, expressed in molar units (e.g. mol/s), whereas $G_E[A]$ and $G_Y[A]$ denote the magnitudes of these streams expressed in mass units (e.g. g/s).

2.3. Thermodynamic characteristics of the reagent system

At the state of thermodynamic equilibrium, the relationship between the concentrations (more precisely: between activities) of the reagents is given by the equilibrium constant. The equilibrium constant of a reversible reaction:

$$aA + bB = cC + dD$$

is formulated as follows:

$$K = \frac{(a_C^*)^c \cdot (a_D^*)^d}{(a_A^*)^a \cdot (a_B^*)^b} \tag{7}$$

a_A^*, a_B^*, a_C^* and a_D^* denote equilibrium reagent activities (in dimensionless form).

The constant K is a thermodynamic equilibrium constant. Its value depends only on the temperature.

In technological calculations, the following form of the equilibrium constant may be used:

$$K_C = \frac{(c_C^*)^c \cdot (c_D^*)^d}{(c_A^*)^a \cdot (c_B^*)^b} \tag{8}$$

c_A^*, c_B^*, c_C^* and c_D^* denote the molar concentrations of reagents at equilibrium.

When the reactants are in the gas phase, the equilibrium constant may be expressed as:

$$K_P = \frac{(p_C^*)^c \cdot (p_D^*)^d}{(p_A^*)^a \cdot (p_B^*)^b} \tag{9}$$

p_A^*, p_B^*, p_C^* and p_D^* denote the partial pressures of the reagents at equilibrium.

2.4. Kinetic characteristics of the chemical process

2.4.1. Kinetics of chemical reactions

The rate of reaction is defined as the amount of the substrate processed or the amount of product produced per unit of time in a unit of volume of the system. For the reaction 1A = 1B, its average reaction rate over time, $\Delta\tau$, can be expressed by the following equation:

$$\overline{r} = \frac{1}{v_R} \cdot \frac{\Delta n[A]}{\Delta\tau}, \left[\frac{\text{mol}}{m^3 \cdot s}\right] \quad (10)$$

Δn[A] is the amount of substrate A which was processed in time Δτ and $\mathcal{V}_R$ is the effective volume of the reactor (filled with the reagents). The symbol $\overline{r}$ denotes the average reaction rate related to the total active volume of the reactor $\mathcal{V}_R$ and for the duration of the process, Δτ. As the reaction rate may change during the process, the value of the instantaneous (actual) reaction rate may be used:

$$r = \pm \frac{1}{v_R} \cdot \frac{dn_i}{d\tau}, \left[\frac{\text{mol}}{m^3 \cdot s}\right] \quad (11)$$

where n_i is the number of moles of substrate A or product B.

2.4.2. Kinetic equation

The kinetic equation expresses the dependence of the reaction rate on the concentration of reagents and temperature.

For a reaction: aA + bB = products

the kinetic equation can be expressed as:

$$r = k \cdot c_A^a \cdot c_B^b \quad (12)$$

where c_A and c_B are the molar concentrations of the substrates.

The reaction rate constant, k, does not depend on the concentration of the reagents but depends on the temperature. The sum of exponents a + b is called the order of the reaction.

2.4.3. Reaction rate

If reaction 1A → 1B proceeds in a closed system with a constant volume, then the actual number of moles of the substrate, n[A], can be found from the following equation:

$$n[A] = n_0[A] \cdot (1 - x) \quad (13)$$

$n_0[A]$ – the initial number of moles of reagent A,

x – the conversion of this component.

After dividing equation (13) by the effective volume, $\mathcal{V}_R$ of the reactor, the dependence of molar concentration, c_A, on the conversion, x, may be found:

$$c_A = c_{A0} \cdot (1 - x) \quad (14)$$

c_{A0} is the concentration of substrate A when x = 0.

In the case of an irreversible first order reaction, the following equation may be used to expresses the dependence of the reaction rate on the conversion:

$$r = k \cdot c_{A0} \cdot (1 - x) \quad (15)$$

Because in the initial state, at $x = 0$, the reaction rate $r = r_0$, the relationship (15) can be used in the form:

$$r = r_0 \cdot (1 - x) \qquad (16)$$

The reaction rate constant, k, depends on the temperature, and this also applies to the value of r_0. Equation (16) shows the dependence of the 1st order irreversible reaction rate on the conversion at a given temperature and initial substrate concentration.

The dependence of the reaction rate on the conversion may be used in the case of an irreversible reaction of the n^{th} order, whose kinetic equation can be written as:

$$r = k \cdot c_A^n \qquad (17)$$

$$\text{or} \quad r = r_0 \cdot (1 - x)^n \qquad (18)$$

where: $r = r_0$, when $x = 0$

If the reaction is reversible (e.g. A = B), then the observed reaction rate is the result of two opposite reactions: $\vec{r}$ (reaction A→B) and $\overleftarrow{r}$ (reaction B→A). The resultant reaction rate, r, is the difference in the rate of these reactions:

$$r = \vec{r} - \overleftarrow{r} \qquad (19)$$

The kinetic equation of a reversible reaction with the stoichiometric equation

$yA \leftrightarrow zB$ can be expressed as

$$r = \vec{k} \cdot c_A - \overleftarrow{k} \cdot c_B \qquad (20)$$

where: $\vec{k}$ and $\overleftarrow{k}$ are reaction rate constants of reactions occurring in opposite directions.

2.4.4. Influence of temperature on reaction rate

According to the Arrhenius theory, the influence of temperature on the reaction rate constant, k, is expressed by the equation:

$$k = k_m \cdot \exp\left(-\frac{E}{RT}\right) \qquad (21)$$

R - gas constant, [8.31 J/(mol·K)],

T - temperature, [K],

k_m - the maximum value of constant k,

E - activation energy of the reaction, [J/mol].

As follows from equation (21), two quantities affect the kinetics of a chemical reaction: the factor, k_m, and the activation energy, E.

The Arrhenius equation may be expressed in the logarithmic form:

$$\ln k = \ln k_m - \frac{E}{RT} \tag{22}$$

In the graph with coordinates (T^{-1}, ln k) this relationship has the form of a straight line, whose slope is the steeper, the greater the activation energy, E (Fig.2.1).

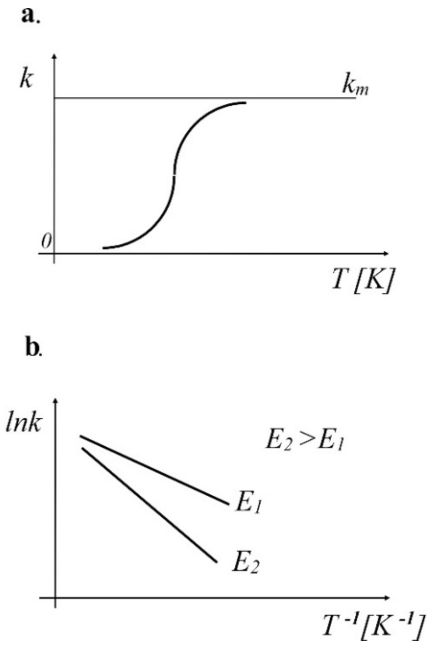

Fig. 2.1. The Arrhenius law; influence of temperature T, [K], on the reaction rate constant, k. E_1, E_2 - activation energy of reactions 1 and 2.
k_m – maximum value of the rate constant, k, when the temperature approaches infinity.

CHAPTER 3

TECHNOLOGICAL BALANCES AND PROCESS EQUATIONS

3.1. Mass balances

The technological balance of a chemical plant consists of a number of equations, which describe the flow of mass or energy (enthalpies) streams supplied to and discharged from the installation or one of its parts. These equations have the form: input = output (I = O). For each of the pieces of apparatus, which take part in the process, the balance equation I = O may be written, which takes into account the presence of the element in each of the streams, regardless of the form in which it occurs. The size of streams in the balance equations refer to a specific basis of the balance, which can be e.g. the volume of daily (hourly, annual) production. The technological balance may apply to the entire installation or to its selected part e.g. one or several pieces of apparatus. This may be indicated by showing a specific control area (CA) within the scheme of the installation. The balance equations include all the streams flowing across the boundaries of the selected control area CA.

3.1.1. Mass balance of a continuous process

In a reactor operating in a continuous manner (Fig. 3.1), the balance equations for element A contained in stream E entering the system and in the discharge stream, Y, are:

$$W_E[A]\cdot\Delta\tau \;=\; W_Y[A]\cdot\Delta\tau + \Delta n[A] \qquad (1)$$

$$G_E[A]\cdot\Delta\tau \;=\; G_Y[A]\cdot\Delta\tau + \Delta m[A] \qquad (2)$$

Symbols $W_E[A]$ and $W_Y[A]$ denote the stream of element A streams flowing across the boundaries of control area CA. In equation (1), the magnitude of the introduced stream, E, and discharged stream, Y, is expressed in molar units, e.g. [mol/s]. The symbols $G_E[A]$ and $G_Y[A]$ in equation (2) indicate the intensity of the same streams expressed in mass units, e.g. [g/s]. The other symbols:

$\Delta\tau$ [s] – period of time, to which the balance relates
Δn [mol] – change in the number of moles of element A (positive or negative) in control area CA over the period $\Delta\tau$
Δm [g] – change of mass of element A (positive or negative) in control area CA during the period $\Delta\tau$.
When the process takes place under steady conditions, the amount of each of the components within control area CA does not change over time, i.e.
$\Delta n[A] = 0$
$\Delta m[A] = 0$

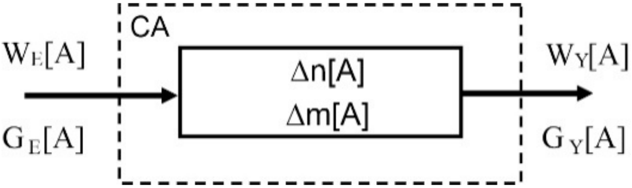

Fig. 3.1. Scheme of a flow through reactor in a continuous process.
W[A] and W[B] - streams of substrate, A, and product, B, CA - control area,
T- temperature, E - introduced stream, Y - discharged stream.
Δn [mol] - change in the number of moles of element A, in the control area CA over the period $\Delta\tau$.
Δm [g] - change of mass of element A in control area CA during the period $\Delta\tau$.

3.2. Enthalpy balances

The organization of production processes depends on the energy effect of the occurring reactions. In the case of endothermic reactions, the necessary energy is supplied from external sources. Installations in which exothermic processes are carried out are self-sufficient in terms of the energy balance, and when a significant excess of heat is obtained, it can be used for various purposes. The economic value of the enthalpy contained in a material depends on the temperature at which it can be transferred. The enthalpy contained in high temperature materials can be used for many purposes. In contrast, the enthalpy of low temperature materials can not be used. It is transferred out from the installation with the use of refrigerants, e.g. air or water. The energy management in a production installation can be shown in the form of an energy balance.

If the process in a production installation takes place under constant pressure, its enthalpy can be used as a measure of the energy contained in the processed materials. Enthalpy occurs in two forms. The first is the enthalpy due to the temperature of the material. The second form is the enthalpy of formation of the substances contained in the material, resulting from their molecular structure and state of aggregation. Basing on the enthalpy of reagent formation, the thermal effect of the reactions can be calculated. The enthalpy of exothermic reactions is usually expressed as a negative number.

3.2.1. Enthalpy of heating

The enthalpy of heating, Δh, of a substance with mass m and temperature T may be determined as:

$$\Delta h = m \cdot c \cdot (T - T_0) \ [J] \tag{3}$$

m - mass of material, [g],

c - specific heat under constant pressure, [J/(g·°C)],

T - temperature, [°C],

T_0 - the reference temperature [°C], at which the enthalpy of heating is assumed to be zero.

The amount of the material can be expressed in mass units, e.g. [g, kg], or in molar units [mol, kmol]. The quantity m·c [J/°C] is the heat capacity of the material.

The flow rate of a stream of material can be expressed in mass units, e.g. [kg/s] or molar units, e.g. [kmol/s]. The stream of enthalpy of heating, ΔH, carried by a material stream with the flow rate W [kmol/s] or G [kg/s] at temperature T can be expressed as follows:

$$\Delta H = W \cdot C \cdot (T - T_0), \ [J/s] \tag{4}$$

$$\Delta H = G \cdot c \cdot (T - T_0), \ [J/s] \tag{5}$$

where:

C - molar heat capacity at constant pressure, [J/(mol·°C)],

c - specific heat capacity under constant pressure, [J/(g·°C)].

The quantities W·C [J/(°C·s)] and G·c [J/(°C·s)] express the heat capacity of the material stream. Specific heat capacity and molar heat capacity depend on the temperature. In order to simplify the calculations when high accuracy is not required, their average values may be used in the range from the reference temperature, T_0, to the actual temperature of the material stream.

3.2.2. Enthalpy of reaction

In technological calculations, the thermal effect of the reaction is usually treated in the following way: as a result of exothermic reactions there is an increase in heating enthalpy and in the temperature of the reagents; this is recorded on the input side in the heat balance of the process. In contrast, the thermal effect of the endothermic reaction is placed on the output side. When calculating the heat balance of a complex process in which many reactions take place, the total thermal effect of the process, q_R, for all reactions taking place can be represented as the difference between the sum of the enthalpies of the product formation Σ_{prod} and the sum of enthalpies of the substrate formation Σ_{sub}:

$$q_R = \Sigma_{prod} \cdot [n_i \cdot (-\Delta Q_i)] - \Sigma_{sub} \cdot [n_i \cdot (-\Delta Q_i)], \text{ [J]} \qquad (6)$$

n_i - number of moles of reagent i (substrate or product),

ΔQ_i - enthalpy of formation of reagent i, [J/mol].

Equation (6) applies to all reagents involved in the reaction.

For this calculation, the enthalpy of reagent formation should be used, which is determined at the temperature chosen as the reference temperature.

3.3. Process equations

The process equations are used for describing the course of processes in the production apparatus: reactors, heat exchangers, mass exchangers, etc. These equations present relationships between values, called process variables, e.g. reagent concentrations, their temperature, conversion, reaction rate, etc. Process equations are derived from mass or enthalpy balances.

As an example, the case of an adiabatic process carried out in a tubular reactor with a plug flow of reactants is presented (Fig. 3.2). In the reactor an exothermic reaction 1A = 1B takes place, whose enthalpy is equal to Q_R [J/mol]. A stream with the flow rate $W_E[A]$ [mol/s] at temperature T_E containing only substrate A is fed into the reactor. A stream of the mixture of reactants A and B with the intensity W = W [A] + W [B] flows through the reactor.

The process equation which describes the dependence of the temperature of the reactant stream on the conversion can be derived from the mass and enthalpy balances in control area CA, which is separated from the rest of the reactor by an arbitrary boundary perpendicular to the direction of flow (Fig. 3.2). At the boundary of control area CA, the total flow of the stream of reagents is W[A] + W[B], the conversion is x and the temperature is T.

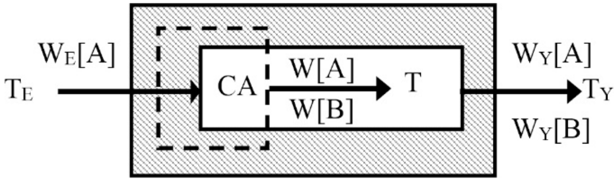

Fig. 3.2. Diagram of a tubular reactor with a plug flow of reactants operating under adiabatic conditions. W[A] and W[B] – flow rate of the substrate and product.

For this reaction, the following results may be derived from the process equation:

$$W[A] = W_E[A]\cdot(1-x),\ [mol/s], \qquad (7)$$

$$W[B] = W_E[A]\cdot x,\ [mol/s]. \qquad (8)$$

The amount of enthalpy produced in control area CA can be expressed as:

$$Q_{RS} = W_E[A]\cdot x\cdot Q_R,\ [J/s]. \qquad (9)$$

Assuming the reference temperature is T_0 and denoting the average molar heat of the reagents with the symbols $\overline{C}_A$ and $\overline{C}_B$, the balance equation for control area CA, may be obtained, where T is the temperature of the stream leaving control area CA:

$$W_E[A]\cdot \overline{C}_A\cdot(T_E - T_0)+W_E[A]\cdot x\cdot Q_R=$$
$$=W_E[A]\cdot(1 - x)\cdot \overline{C}_A\cdot(T - T_0)+W_E[A]\cdot x\cdot \overline{C}_B\cdot(T - T_0) \qquad (10)$$

Basing on equation (10), it is possible to derive a process equation that expresses the dependence between the temperature, T, of the reactants and the conversion, x, in a plug flow reactor operating under adiabatic conditions:

$$T = \frac{\overline{C}_A\cdot(T_E - T_0) + x\cdot Q_R}{\overline{C}_A + x\cdot(\overline{C}_B - \overline{C}_A)} + T_0 \qquad (11)$$

In the case of a process carried out under adiabatic conditions, the changes in temperature of reactants depend on the enthalpy of the reaction and the molar heat of the reactants.

CHAPTER 4

CHEMICAL PROCESSES IN MULTIPHASE SYSTEMS

4.1. Properties of heterogeneous systems

In many chemical processes, reagents occur as two distinct phases. In such systems, chemical transformations occur on the surface, which separates the reactants, i.e. on the phase boundary. The rate of such reactions is influenced by transport of reagents e.g. transfer of substrates towards the interface and transfer of products in the opposite direction.

An example of a process occurring in a heterogeneous system is the combustion of coal in a stream of gases containing oxygen. In a system with an excess of oxygen relative to the amount of carbon, the process consists of three stages:

- transport of the gaseous substrate (O_2) from the gas phase to the carbon surface,
- a chemical reaction taking place on the carbon surface:

$$C + O_2 = CO_2$$

- transport of the product (CO_2) from the gas layer at the carbon surface into the bulk gas phase.

The first and third stages of the process have a significant impact on the rate of the combustion process.

In heterogeneous systems, the rate of processes depends on the specific surface area (σ). This is the size of the interface per unit of volume of the system

$$\sigma = \frac{F_I}{V}, [m^{-1}] \tag{1}$$

F_I - the interface area [m^2], V - overall system volume, [m^3].

The rate of transformation occurring in heterogeneous systems (r_F) may be referenced to a unit of the reactant interface:

$$r_F = \pm \frac{1}{F_I} \cdot \frac{dn_i}{d\tau}, \left[\frac{mol}{m^2 s}\right] \tag{2}$$

n_i amount of substrate or product [mol], τ time, [s]

The relationship between the reaction rate, r_F, and the reaction rate per unit of volume of the system, r_V, can be expressed as:

$$r_V = \sigma \cdot r_F, \quad \left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}}\right] \tag{3}$$

where σ denotes the specific surface area of the reagent system.

4.2. Dissolution of a solid in a liquid

Dissolution of solid materials in liquid solvents is usually carried out in tanks with agitators, which put the liquid into turbulent motion. Under such conditions, the composition of the liquid in the entire volume is almost uniform. However, even with intensive mixing, the flow in the thin layer at the solid surface is laminar. In such a layer, the transfer of liquid components proceeds by molecular diffusion. The substance being dissolved diffuses from the solid phase surface through the laminar layer towards the bulk of the liquid, where the flow is turbulent.

The measure of the diffusion rate (r_D) is the amount of substance A (n_A [mol]) that diffuses by a unit of surface (F_D [m^2]) per unit of time (τ [s]):

$$r_D = \frac{1}{F_D} \cdot \frac{dn_A}{d\tau}, \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}}\right] \tag{4}$$

In accordance with Fick's law, the diffusion rate is directly proportional to the concentration gradient of the diffusing component (dc_A/dz) and to the diffusion coefficient, D, whose value depends on the properties of the solution composition and on the temperature.

$$r_D = -D \cdot \frac{dc_A}{dz}, \left[\frac{\text{mol}}{\text{m}^2\text{s}}\right] \tag{5}$$

D - diffusion coefficient, characteristic for a given system, [m^2/s],
c_A - molar concentration of the diffusing component A, [mol/m^3],
z - distance along the diffusion path, [m].

Hydrodynamic conditions affect the rate of dissolution. This may be shown using a simplified model of the boundary layer, in which the movement is laminar (Fig. 4.1). It is assumed that there is a sharp boundary between the laminar layer and the turbulent movement volume. In real systems there is a transition zone, which is omitted here for simplicity. The distribution of the concentration of the dissolved component A near the boundary between the solution of A in solvent B and the solid phase A results from the following assumptions:

(1) there is ideal mixing in the turbulent flow area,
(2) in the boundary layer, the decrease in the concentration of component A is linear, i.e. the concentration gradient of A in this layer has a constant value, and therefore:

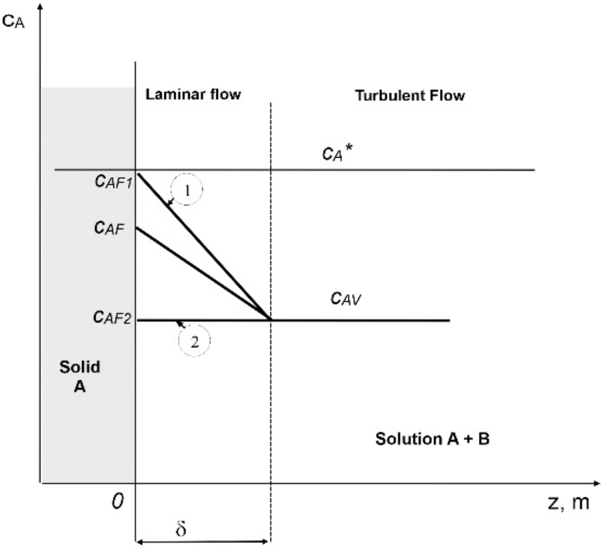

Fig. 4.1. Dissolving of solid A in a liquid solvent B. c_{AV} – concentrate on of A, [mol/m^3], in the volume of solution with turbulent flow,
c_{AF} - concentration of A, [mol/m^3], in the solution layer at the solid phase surface,
c_A* - concentration of A in a saturated solution, δ - boundary layer thickness, [m],
z - distance from the solid surface.

$$\frac{\mathrm{d}c_A}{\mathrm{d}z} = -\frac{c_{\mathrm{AF}} - c_{\mathrm{AV}}}{\delta}, \ [\frac{\mathrm{mol}}{m^4}] \tag{6}$$

- c_{AV} concentration of A, [mol/m^3], in the volume of solution with turbulent flow,
- c_{AF} concentration of A, [mol/m^3], in the solution layer at the solid phase surface,
- boundary layer thickness, [m].

It is assumed that the rate of the transport of component A, r_F, from the solid phase surface to the liquid can be expressed with a kinetic equation of a first order reaction with a constant rate, k. The rate of the transport of component A (related to a unit of the interface) is determined by the relationship:

$$r_F = k\,(c_A^* - c_{AF}),\quad \left[\frac{mol}{m^2 \cdot s}\right] \tag{7}$$

In the extreme case when $c_{AF} = c_A^*$, there is a state of equilibrium between the liquid and solid phases at the surface of the solid, and the rate of the process is zero.

On the basis of Fick's law and equation (6), the diffusion rate, r_D, can be determined:

$$r_D = D\,\delta^{-1}(c_{AF} - c_{AV}),\quad \left[\frac{mol}{m^2 \cdot s}\right] \tag{8}$$

If the process proceeds under steady state conditions, then $r_F = r_D$. Hence:

$$k\,(c_A^* - c_{AF}) = D\,\delta^{-1}(c_{AF} - c_{AV})$$

This relationship can be used to determine the concentration, c_{AF}:

$$c_{AF} = \frac{k\,c_A^* + D \cdot \delta^{-1} c_{AV}}{k + D \cdot \delta^{-1}} \tag{9}$$

By entering the result from equation (9) into equations (7) and (8), the following relationship may be obtained:

$$\left.\begin{matrix} r_F \\ r_D \end{matrix}\right\} = \frac{k\,D\,\delta^{-1}}{k + D\,\delta^{-1}}(c_A^* - c_{AV}) \tag{10}$$

This result applies to processes taking place under steady state conditions. There are two extreme cases:

1. when $k \gg D\,\delta^{-1}$, then $r_F = r_D = D\,\delta^{-1}(c_A^* - c_{AV})$

In this case there are significant limitations in the process of transferring components through the laminar layer e.g. due to the slow mixing of liquids (high δ value). As such, the rate constant, k, has no significant effect on the rate of the process, and $c_{AF1} \approx c_A^*$ (Fig. 4.2). Since the diffusion of reagents has a decisive impact on the process, its rate strongly depends on the hydrodynamic conditions.

2. when $k \ll D\,\delta^{-1}$, then $r_F = r_D = k\,(c_A^* - c_{AV})$

At a low k value and under favourable mass transfer conditions, mass transfer limitations do not play a significant role, and the concentration of c_{AF2} equals the concentration of c_{AV} in bulk liquid phase (Fig. 4.2). Then the rate of the dissolution process depends only on the rate of transfer of component A from solid to liquid at the phase interface.

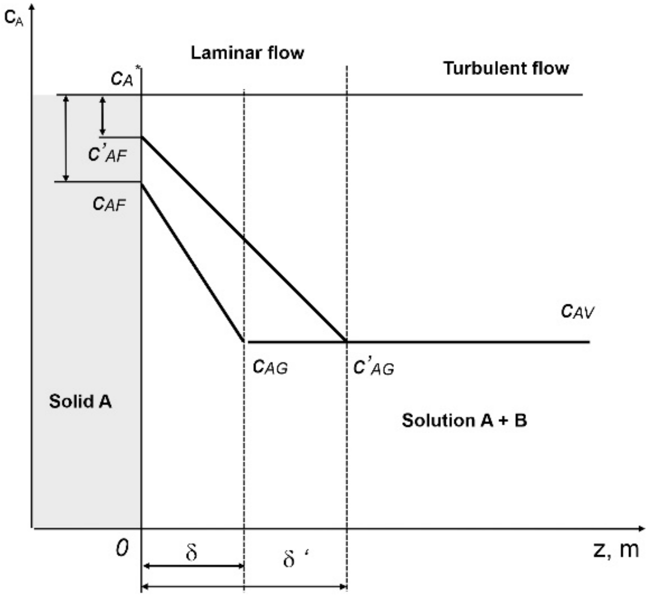

Fig. 4.2. The impact of hydrodynamic conditions on the dissolution of solid A in a liquid solvent B, c_{AV} - concentration of A, [mol/m^3], in the volume of solution with turbulent flow, c_{AF} - concentration of A, [mol/m^3], in the solution layer at the solid phase surface, δ - boundary layer thickness, [m], z - distance from the solid surface.

In actual systems, there are usually intermediate situations between these extreme cases. Hydrodynamic conditions generally affect the course of these processes (Fig. 4.2). When the velocity of the motion of a liquid decreases, the thickness of the boundary layer increases, which has the following results:

the concentration gradient of component A decreases (smaller slope of segment c'_{AF} c'_{AG}),

the concentration of component A at the solid phase surface increases ($c'_{AF}>c_{AF}$),

the diffusion rate of component A through the laminar layer decreases.

4.3. Crystallization from liquid solutions

The course of the crystallization of a solid from a liquid solution is shown in Fig. 4.3. Line E shows the composition of the saturated solution of substance A in solvent B. Crystallization of substance A from its homogeneous solution can start when the solution is in a supersaturated state (at the area above line M). In the first stage, nucleation of substance A takes place. At the beginning, nuclei do not have a well-developed crystal structure, which is formed in the course of crystal growth. The formation of nuclei occurs under conditions of supersaturation of the solution (the area above line M).

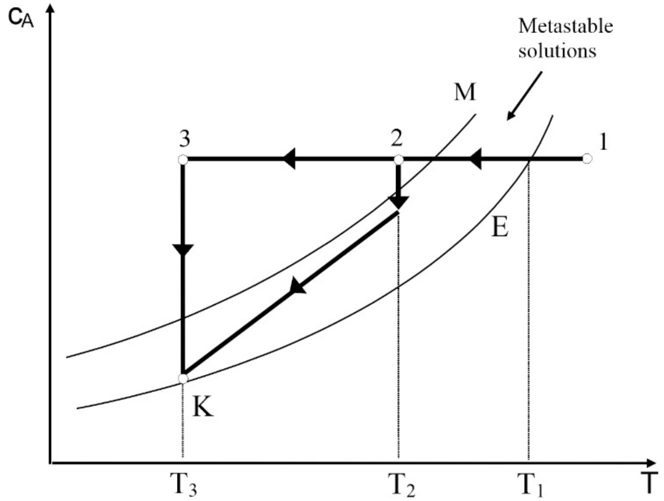

Fig. 4.3. Crystallization of a solid product from a liquid solution.
Line E shows the composition of the saturated solution of substance A. Line M shows the upper limit of the supersaturated state of the solution
c_A - concentration of the component A, T - temperature.

When the composition of the solution is located in the area between curves E and M, although the solution is supersaturated, no solid phase nuclei may be formed. In such solutions, which are referred to as metastable, crystallization occurs only through the growth of existing crystals.

The rate of crystallization depends on the extent of supersaturation of the solution, γ, which is defined as follows:

$$\gamma = \frac{c - c^*}{c^*}$$

c - concentration of the dissolved component,
c* - its concentration in a saturated solution.

The dependence of the crystals growth rate on solution supersaturation is shown in Fig. 4.4 (line K). In the supersaturated solution, crystal nuclei can be formed when the degree of supersaturation is not less than that at line M. The rate of nucleus formation increases with the increase in concentration (line Z).

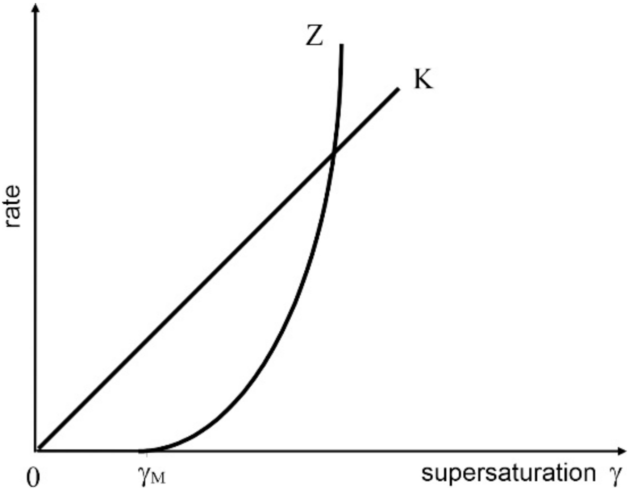

Fig. 4.4. The dependence of the crystals growth rate on solution supersaturation. Z – rate of nucleus formation, K – crystals growth rate, γ – supersaturation of the solution, γ_M – limit of supersaturated solutions.

This property of solutions can be used to control the crystallization process. When a fine crystalline product should be produced, crystallization is carried out at high solution supersaturation. Then a large number of nuclei are formed and small crystals may be produced. In order to obtain a product of large crystals, the process is carried out in such a way that after the formation of the first nuclei, the crystallization is carried out under the conditions of a metastable solution, in which no new nuclei are formed. At the same time the crystals formed at the beginning may grow. Two different ways of carrying out crystallization are presented in Fig. 4.3. Solid substance A is dissolved at high temperature to obtain a highly concentrated solution (point 1). When this solution is quickly cooled to T_3, the state of significant supersaturation (point 3) is reached, in which numerous nuclei are produced. By this procedure, a fine crystalline product may be obtained. After crystallization, a saturated solution at T_3 (point K) remains in the liquid phase.

When a product with large crystals is desired, the solution in its initial state (point 1) is cooled only to temperature T_2, at which the solution is supersaturated, but only to a small extent, so that only few nuclei are produced. The nucleation process ends when the composition of the solution reaches the level corresponding to curve M. By slowly cooling such a solution, crystallization is carried out in a metastable solution, up to point K. In that way, large crystals may be obtained.

4.4. Systems of two solid phases and a gas phase

In many industrial processes, chemical reactions occur in systems consisting of solid and gaseous reagents. One of them is the decomposition of a solid, A_S, into a solid product B_S, and a gas product, C_G:

$$A_S = B_S + C_G,$$

An example of this process, is the decomposition of calcium carbonate in the production of quicklime:

$$CaCO_3 = CaO + CO_2 \qquad \Delta H^0_{298} = 163.7 \text{ kJ} \qquad (11)$$

It is an endothermic, reversible reaction with the equilibrium constant:

$$K_p = p^*_{CO2}, \ [Pa]$$

When reaction (11) is at equilibrium, the CO_2 pressure has a definite value at each given temperature (Fig. 4.5). If the CO_2 pressure is higher, the only stable solid component is $CaCO_3$. On the other hand, at a pressure lower than the equilibrium pressure, only CaO is stable solid.

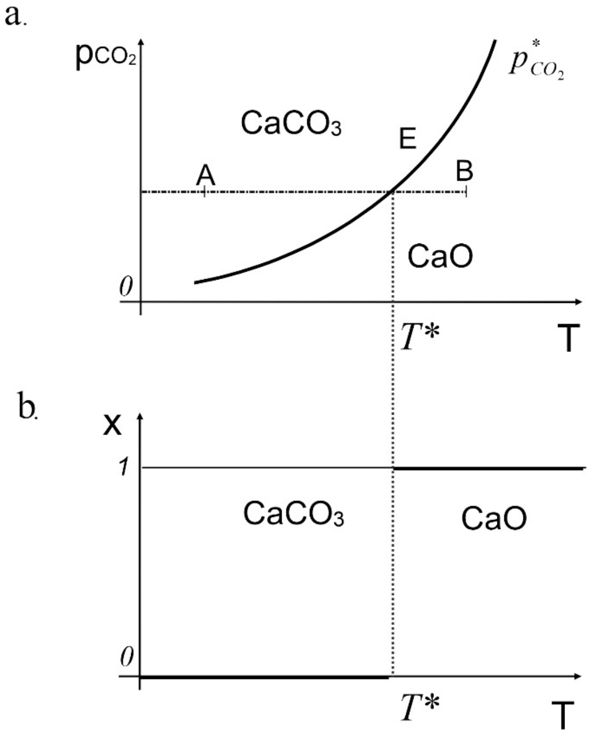

Fig. 4.5. A system consisting of $CaCO_3$, CaO and CO_2 at equilibrium
E - equilibrium line, A - area of $CaCO_3$ stability, B - area of CaO stability,
T - temperature, T^* - temperature of equilibrium state, p^*_{CO2} - CO_2 pressure in equilibrium state, p_{CO2} - CO_2 pressure.

If $CaCO_3$ is the only component at the start of reaction (11), conversion, x, is defined as follows:

$$x = \frac{n[CaO]}{n[CaCO_3] + n[CaO]}$$

where: $n[CaCO_3]$ and n[CaO] indicate the number of moles of these components in the system.

If the pressure of CO_2 and the temperature correspond to the area of stability of calcium carbonate (e.g. point A in Fig. 4.5a), then both components, $CaCO_3$ and CO_2, are stable. The decomposition of calcium carbonate is possible when the temperature is higher than the equilibrium temperature, T* (Fig. 4.5b).

The mechanism of this reaction is complex. Initial transformations occur in the surface layer of $CaCO_3$ crystallites (Fig. 4.6). Some CO_3^{2-} ions in the carbonate crystal structure break down, CO_2 is released, and the corresponding places in the crystal structure are filled by O^{2-} ions. This creates defects in the $CaCO_3$ crystal lattice, although its overall structure remains as it was in the $CaCO_3$ crystal. However, when a significant amount of defects is accumulated in a part of the network, the crystal structure begins to transform and it takes on a form similar to that of calcium oxide. These local transformations cover only a small part of the $CaCO_3$ crystal: however, this gives rise to the nucleation of a new solid phase. At the beginning the domains are small and have an irregular structure, in which many CO_3^{2-} ions are retained.

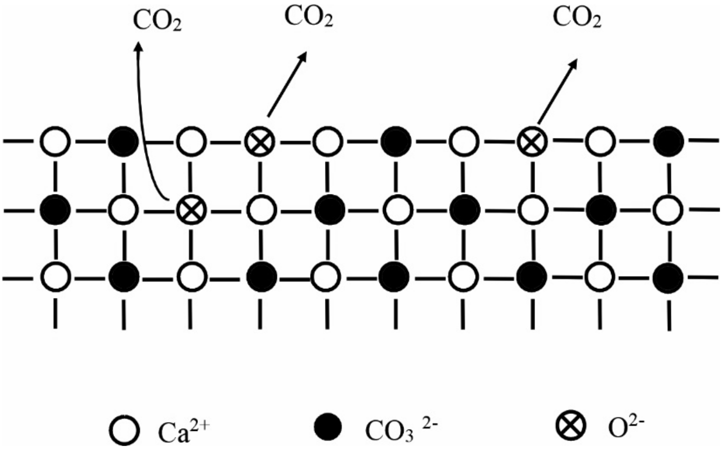

Fig. 4.6. A simplified scheme of $CaCO_3$ crystal lattice during transformation into CaO.

The formation of the first nuclei of the CaO phase begins a new stage of the transformation. Initially, the nuclei are a part of the original calcium carbonate crystal, and their further growth occurs as a result of the transformation of subsequent fragments of this crystal. This takes place at the surface separating the two adjacent solid phases, $CaCO_3$ and CaO. This mechanism affects the kinetics of the process (Fig. 4.7). After a period of slow transformations, when the first nuclei of the CaO phase are produced, the reaction rate increases significantly. It is the faster, the larger the $CaCO_3$/CaO interface. The growing nuclei of the CaO phase transform into regular crystals, which are no longer integrated with the parent crystal and separate from it as separate CaO crystals. At the same time, new nuclei are created that undergo further transformation.

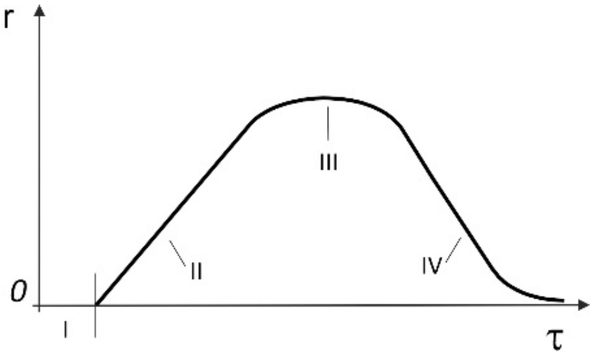

Fig. 4.7. Kinetics of the $CaCO_3$ transformation into CaO. τ - time, r - reaction rate, I - no nuclei are formed, II - CaO nuclei are formed and grow, III - CaO crystals grow, IV - final period of $CaCO_3$ decomposition.

As calcium carbonate is depleted, the rate of nucleation and the rate of decomposition of $CaCO_3$ decreases (Fig. 4.8). The kinetics of this type of processes are characterized by three stages: the initial one, in which the reaction rate is slow, the fast reaction period, and the final, in which the reaction rate decreases until the end of transformation. Many other processes take place in a similar way, in which the solid phase of the substrate is transformed into a new solid phase of the product.

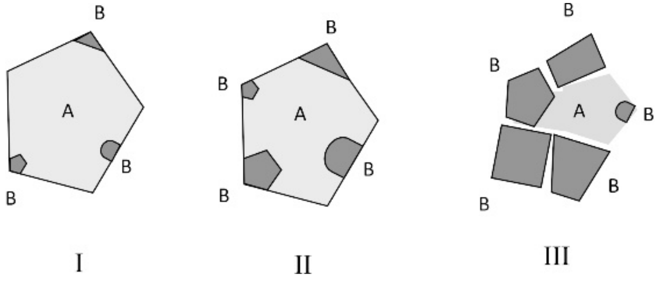

Fig. 4.8. Calcium carbonate decomposition steps; A - $CaCO_3$. B - CaO.
I - CaO nuclei are formed and grow, II - CaO crystals grow and III - separation of CaO nuclei and formation of new ones.