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MACROKINETICS OF CHEMICAL PROCESSES

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I. INTRODUCTION

A characteristic feature of modern chemical processes, occurring at high rates at high temperatures and pressures in multiphase systems, is their great complexity. This complexity is shown in the large number and wide variety of the parameters determining the course of the processes and the large number of internal relations between the parameters and their mutual influence, the change in one parameter entailing a non-linear change in others. The complexity is enhanced by the occurrence of feedback between the parameters and also by the development of competing modes of the process, whereby the course of the latter is altered.

The complexity of a chemical process makes it necessary to understand it in terms of *models*, i.e. systems which reflect the individual aspects of the phenomena in a given process, restricted to the required conditions. Models are represented in terms of a definite mathematical notation, which establishes the relation between the parameters of the process, using both theoretical methods and experimental data. In their analysis and use, such models are usually divided into separate blocks, purely chemical phenomena, determined by classical chemical kinetics, being considered separately; blocks taking into account mass and energy transfer during the chemical reaction are distinguished. In this connection it has become usual to distinguish the micro- and macro-kinetics of chemical processes. This subdivision is of course to a certain extent arbitrary, but it makes

possible an accurate quantitative estimate of various aspects of a complex chemical process, so that it constitutes, in consequence, the scientific basis of industrial chemical processes.

The modern concept of macrokinetics was introduced by Frank-Kamenetskii [1], who also indicated the problems and the scope of this concept. Subsequently macrokinetics were formulated as a special branch of chemical kinetics and became the basis for the calculation of the parameters of chemical reactors and industrial chemical processes. Ten years after the appearance of Frank-Kamenetskii's paper, a special Symposium of the European Federation of Chemical Engineers devoted to the problems of macrokinetics was held in Amsterdam in 1957. [2] With the advent of computer techniques, the macrokinetics of chemical processes have entered a new stage of development — there is now a possibility of mathematically modelling chemical processes, their optimisation, and control [3-5]. The problems of macrokinetics have been further considered in Levich's papers [6].

Microkinetics deal with reactions in a chemical process at the molecular level on a scale not exceeding the mean free path of the molecules. Molecular friction (viscosity), molecular heat transport (thermal conductivity), and molecular matter transport (molecular diffusion) are also included among phenomena on the scale of molecular interactions.

In the study of processes at two levels, the state of liquid media becomes important. The mixing of liquids is called microscopic if it is restricted to the mixing of individual molecules; such a state of the liquid is called a micro-state [7,8]. Classical chemical kinetics are based on kinetic equations corresponding to micro-states.

Macrokinetics are concerned with the study of the interactions in a chemical process at the level of molecular aggregates on the scale of eddies, drops, or gas bubbles, i.e. on the scale of the so-called macro-particles. The mixing of liquids is regarded as macroscopic if it occurs on interaction between macro-particles. Consequently such a liquid state is referred to as macroscopic.

Examination of macro- and micro-mixing is important for heterogeneous systems, since one of the phases in such systems usually behaves as a liquid in a macro-state. For example, the solid phase in liquid–solid systems may be interpreted as a liquid in a macro-state, since each species of the solid constitutes a definite molecular aggregate. The disperse phase in liquid–liquid systems may serve as another example. Segregation in such systems increases with the surface tension.

Homogeneous systems behave as liquids in a micro-state, except for very viscous liquids or systems in which very rapid reactions take place. In the latter two cases the time required for the homogenisation of the system may prove to be appreciable compared with the rate of reaction and therefore the latter is limited by the mixing process.

The principal problem in macrokinetics is to establish the laws governing the transport of matter and energy on the macroscopic level under real conditions of chemical processes. The problem reduces to determining the distribution of concentrations and temperatures in the reactor as a function of the organisation of the reactant streams, heat inflow or outflow, and the effect of diffusion. For example, in contact-catalytic processes in a stationary catalyst bed one examines on the macroscopic level the distribution of temperatures and concentrations in the radial and axial directions in the bed under the usual non-isothermal and non-adiabatic conditions. On the microscopic level under these conditions, one examines the distribution of heat and concentrations within the catalyst particle (and within its pores).

Evidently, in the examination of a chemical process as a whole micro- and macro-kinetics constitute a single unity. However, this does not mean that the problems involved in the study of macrokinetics cannot be of independent interest, by virtue of the specificity of the scale of the objects examined and the specificity of the laws which obtain on macroscopic levels.

Accordingly, the study of chemical processes in industrial reactors comprises two aspects. Under laboratory conditions, the microkinetics of the process are investigated, whereby the reaction mechanism is established and the kinetic equations are derived. Using an experimental reactor of the chosen design, the parameters of the models which determine the macrokinetics of the process are established — the coefficients of longitudinal and radial mixing, the flow conditions, the coefficients of mass and heat transfer, etc. are determined. The micro- and macro-kinetic parameters are then combined into a complete mathematical model from which graphical and numerical relations between all the process parameters may be obtained by the method of mathematical modelling (the principle is that the deformation of the model is not studied using an actual physical model, as in physical modelling, but directly on the mathematical model itself using electronic computers) and the optimum conditions may be found (using the familiar optimisation methods). Thus the study of macrokinetics constitutes the basis of the modern analysis of industrial chemical processes. The mathematical models of chemical processes, taking into account the phenomena of energy and mass transport, which are superimposed on purely chemical phenomena in order to emphasise the importance of and necessity for the study of the problems of the macrokinetics of chemical processes, are examined below.

II. MATHEMATICAL MODELS OF ISOTHERMAL IDEAL REACTORS

It has become customary to examine the operation of real reactors by comparing them with ideal models. Usually the analysis is based on two extreme models: the ideal plug flow model and the ideal backmix flow model. The possibility of choosing such models was first pointed out by Kirillov [9], who gave a quantitative treatment of the elutriation phenomenon. Quantitative estimates of the course of chemical processes in the above models have been made [10,11].

The ideal plug flow model corresponds to the state in which the components are continuously introduced into the reactor and removed from it (Fig. 1); longitudinal and transverse mixing of the medium particles is then completely absent. The residence time of all the particles in the reactor is the same and equal to the ratio of the volume of the reactor to the volume flow rate of the liquid. The composition of the liquid and the reaction rate vary from point to point along the length of the reactor. The relation between the residence time in the reactor and the rate of reaction is established on the basis of the material balance of the reactor.

The following notation will be used: V_A is the influx of reactant A in kmole s^{-1}, V_r the reaction volume in litres, x_A the conversion defined as $x_A = (c_{A_0} - c_A)/c_{A_0}$, c_{A_0} and

c_A are the initial and final concentrations of reactant A in kmole litre^{-1}, and w_{r_A} is the rate of reaction (the rate of conversion of reactant A) in kmole s^{-1}.

For a steady stream and a constant reactor cross-section, one can write, in accordance with Fig. 1,

$$V_A - (V_A + dV_A) + (-w_{r_A})dV_r = 0 \qquad (3)\dagger$$

whence

$$-dV_A + (-w_{r_A})dV_r = 0.$$

Bearing in mind that $V_A = V_{A_0}(1 - x_A)$ and $dV_A = -V_{A_0}dx_A$, we obtain after substitution in Eqn. (3), separation of variables, and integration:

$$\frac{V_r}{V_{A_0}} = \int_0^{x_A} \frac{dx_A}{w_{r_A}}. \qquad (4)$$

On introducing the concentration c_{A_0}, defined as the number of kilomoles per unit volume and the volume per second V_s (in litre s^{-1}), one can write

$$V_{A_0} = c_{A_0}V_s. \qquad (5)$$

Evidently the ratio V_r/V_s, which has the dimensions of time, is the residence time τ_n of the reactant in the reactor, and therefore one can write

$$\tau_n = \frac{V_r}{V_s} = c_{A_0}\int_0^{x_A} \frac{dx_A}{w_{r_A}} \text{ (seconds)}. \qquad (6)$$

In the general case for a reaction of an arbitrary nth order the rate of reaction w_{r_A} can be written thus:

$$-w_{r_A} = kc_A^n = kc_{A_0}^n(1-x_A)^n. \qquad (7)$$

After substitution of Eqn. (7) in Eqn. (6), we obtain

$$\tau_n = \frac{V_r}{V_s} = c_{A_0}\int_0^{x_A} \frac{dx_A}{kc_A^n} = \frac{1}{k}c_{A_0}^{1-n}\int_0^{x_A} \frac{dx_A}{(1-x_A)^n} \text{ (seconds)}. \qquad (8)$$

Tubular reactors with a large tube length : diameter ratio (longitudinal mixing may be neglected) with a turbulent flow of liquid or gas (radial mixing may be neglected in view of the planar velocity profile in turbulent motion) are based on the ideal plug flow model. The plug flow model also fits a periodic reactor, but with respect to the time coordinate and not the length coordinate.

The ideal backmix flow model corresponds to the state in which it is assumed that the components are continuously introduced into and removed from the reactor (at the same rate); the mixing of the medium particles in the reactor is so complete that the concentration of each component is the same throughout the volume.

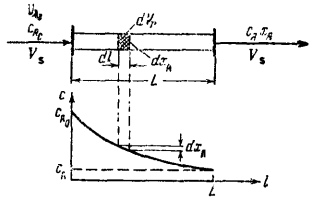


Fig. 1. The structure of the ideal plug flow reactor model.

According to the material balance equation for this model, we have

$$V_s(c_{A_0} - c_A) = (-w_{r_A})V_r. \qquad (9)$$

By analogy with Eqn. (6), the residence time of the reactant in the reactor τ_n' can be represented by the expression

$$\tau_n' = \frac{V_r}{V_s} = \frac{c_{A_0} - c_A}{(-w_{r_A})} = \frac{c_{A_0} - c_A}{kc_A^n} = \frac{1}{k}c_{A_0}^{1-n}\frac{x_A}{(1-x_A)^n}. \qquad (10)$$

Comparison of the conversions in ideal plug flow and ideal backmix flow models of the reactor for the same residence time and a first-order reaction with $k = 1$ yields the curves in Fig. 2. It follows from the graph that in an ideal backmix flow reactor the conversion x_A is lower than in an ideal plug flow reactor. Thus a conversion of 0.85 in an ideal plug flow reactor can be attained in 19 min while in an ideal backmix flow reactor the time required is 57 min.

We may note that, when the reaction medium passes through the plug flow reactor, the conversion increases along the length of the reactor and, since for simple reactions the rate decreases with conversion, the average rate is between the maximum value at the inlet to the reactor and the minimum value at the outlet. When the reaction medium passes through the backmix flow reactor, the conversion at each point in the reactor corresponds to the conversion at the outlet and the average rate is equal to the low value at the outlet from the reactor. Consequently, when the two reactor models are compared under isothermal conditions for the same conversion at the outlet, the average reaction rate in the plug flow reactor is always higher and therefore the required volume of a reactor of this type is smaller.

The model of the reactor affects not only the conversion but also the distribution of the reaction products. We shall examine as an example the decomposition of a component A which can occur in two ways [12]:

$$a_1A \xrightarrow{k_1} R \text{ (desired product)}$$
$$a_2A \xrightarrow{k_2} S \text{ (undesired product)}$$

at rates defined by Eqns. (11) and (12):

$$w_{r_R} = \frac{dc_R}{d\tau} = k_1c_A^{a_1} \qquad (11)$$

$$w_{r_S} = \frac{dc_S}{d\tau} = k_2c_A^{a_2}. \qquad (12)$$

On dividing Eqn. (12) by Eqn. (11), we obtain the ratio of the rates of formation of products S and R:

$$\frac{w_{r_S}}{w_{r_R}} = \frac{k_2}{k_1}c_A^{a_2-a_1}. \qquad (13)$$

It follows from Eqn. (13) that only by varying the concentration c_A is it possible to change the product concentration ratio c_S/c_R, since the kinetic parameters k_1, k_2, a_2, and a_1 are constant for a given system at a given temperature.

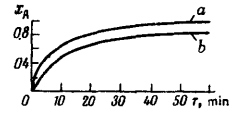


Fig. 2. Conversion in ideal plug flow (curve a) and ideal backmix flow (curve b) models.

† Eqns. (1) and (2) are missing in the Russian original (Ed. of Translation).

Their influence on the distribution of products is shown as follows.

1. If $a_1 > a_2$, i.e. the reaction order for the desired product is higher than the reaction order for the undesired product, then $a_2 - a_1$ is negative. According to Eqn. (13), to obtain relatively high yields of the desired product R, it is necessary to have a high concentration of the reactant A (c_A) in the reactor, which can be achieved in one of the following ways: (a) by using an ideal plug flow reactor, where the concentration c_A decreases gradually from initial high values; (b) by increasing the total pressure in gas-phase systems or by eliminating inert impurities, whereby the concentration of the reactant at the inlet to the reactor is increased; (c) by eliminating the product recycle flow.

2. If $a_1 < a_2$, i.e. the reaction order for the desired product is lower than for the undesired product, the preferential formation of the product R requires lower concentrations of the reactant, which is achieved by one of the following procedures: (a) by using an ideal backmix flow reactor in which the concentration of the reactant rapidly attains the minimum value corresponding to the outlet; (b) by introducing a recycle flow, whereby the inlet concentration and the concentration of reactant A in the reactor are reduced; (c) by reducing the pressure or increasing the concentration of inert gases in gas-phase systems. All these measures necessitate a large reactor. In this case the optimum design is achieved by comparing the economic balance of the cost of removal of the undesired product and the large capital outlay required for larger plant.

3. If $a_1 = a_2$, i.e. both reactions are of the same order, Eqn. (13) becomes

$$\frac{w_{r_S}}{w_{r_R}} = \frac{dc_S}{dc_R} = \frac{k_2}{k_1} = \text{const} \qquad (14)$$

i.e. the distribution of products is constant for a given rate constant ratio k_2/k_1 and independent of the type of reactor. The ratio of the products may be varied by changing the ratio k_2/k_1 in the following way: (a) by changing the temperature conditions of the process, when the activation energies for the two reactions differ from one another; (b) by using a selective catalyst.

Fig. 3 shows the variation of the relative yield of the intermediate product R with the kinetic parameters and the type of reactor [12] for the consecutive reaction

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S.$$

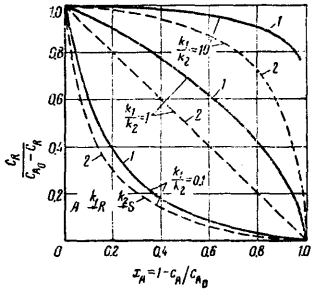


Fig. 3. Relative yield of the intermediate product in ideal plug flow (curve 1) and ideal backmix flow (curve 2) reactors for various conversions of the starting material.

On the basis of Fig. 3, we may conclude firstly, that the yield of the intermediate product R in the plug flow reactor is always higher than in the backmix flow reactor, and, secondly, that for high k_1/k_2 ratios the conversion is high, and vice versa for low ratios, i.e. under these conditions recycle flow should and should not be used respectively.

The distribution functions for the products of parallel consecutive reactions can be very conveniently and rapidly analysed by analogue computers. Structured assembly schemes have been proposed for the solution of problems of this kind by analogue computer; typical chemical reactions have been examined and the optimum yields of products have been calculated [13].

III. MATHEMATICAL MODELS OF ISOTHERMAL NON-IDEAL REACTORS

1. General Postulates

In contrast to the ideal reactors examined above, in non-ideal reactors the distribution of the reacting particles of the medium along the stream and along the stream cross-section is non-uniform. For this reason, in such reactors account must be taken of the transverse and longitudinal mixing of the medium particles. The distribution function of concentrations with respect to time is used as one of the characteristics in the operation of non-ideal reactors. A second characteristic is the state of segregation of the particles, i.e. a distinction must be drawn between processes at a micromixing level (at a molecular level) and processes at a macromixing level (the level of molecular aggregates). The level corresponding to the state of the system is defined by the so-called degree of separation of the system or the degree of segregation I introduced by Danckwerts [7]. The concepts of the "concentration at a point" and the "age of the liquid at a point" are introduced in connection with the concept of the degree of segregation. They denote the concentration, or age, averaged over a very small space compared not only with the system as a whole but also compared with the dimensions of the molecular aggregates and yet large enough to contain many molecules.

If the age of a molecule is defined as the time τ elapsed from the instant when the molecule entered the system, the variance of the age of all the molecules of the system, i.e. the average square of the deviations of the molecular ages from the average age, may be calculated:

$$\text{Var}\,\tau = \overline{(\tau - \overline{\tau})^2}, \qquad (15)$$

where $\overline{\tau}$ is the average age of all the molecules present in the system at a given instant; the overall bar over the symbols denotes an average value for all the molecules.

If the average molecular age at each "point" is denoted by τ_p, the variance of the age may serve as a measure of the degree of separation. The variance is

$$\text{Var}\,\tau_p = \overline{(\tau_p - \overline{\tau})^2}, \qquad (16)$$

where the overall bar denotes averaging over all the points.

If mixing takes place at a molecular level, the average age of all the molecules at each point is the same and equal to the average in the system and the variance of the age at different points is then zero.

If mixing takes place at a macroscopic level, i.e. the system is completely separated (segregated), the variance

of the age at different points in the system is equal to the variance of the age of all the molecules, i.e.

$$I = \frac{\mathrm{Var}\,\tau_p}{\mathrm{Var}\,\tau} = 1. \quad (17)$$

For any other degree of separation, I will be less than unity:

$$I = \frac{\mathrm{Var}\,\tau_p}{\mathrm{Var}\,\tau}\frac{\overline{(\tau_p - \bar{\tau})^2}}{(\tau - \bar{\tau})^2} < 1. \quad (18)$$

The limiting value $I = 0$ corresponds to the state of maximum mixedness, a concept introduced by Zwietering[8].

For a system in which the distribution of residence times is equal to the distribution in an ideal backmix flow model, I may be between zero (mixing at a molecular level) and unity (complete segregation). In a system corresponding to the ideal plug flow model, where there is no mixing of the stream particles, the degree of separation attains the maximum value $I = 1$.

We shall determine the effect of the level of mixing, or the state of the system, on the conversion in the reactors. Consider two arrangements of two reactors corresponding to two extreme models: the ideal plug flow and ideal backmix flow models connected in series (Fig. 4). The difference between the two schemes consists in the fact that in scheme *a* mixing takes place at a later stage and in scheme *b* at an earlier stage. The overall distribution of residence times in both reactor arrangements will be the same — the usual delta-function (see below) is obtained for the plug flow zone and an exponential function for the backmix flow zone.

If these two systems are regarded solely as different types of flow apparatus without chemical reaction, designed, for example, to lower the temperature and concentration variation in a steady stream of liquid, their effects will be completely the same. The difficulty in the study of chemical reactors arises from the fact that usually the mixing of the elements of the liquid takes place at the same time as the chemical reaction. Although the overall mixing in both systems is the same, the mixing in the second scheme takes place at an earlier stage of the chemical reaction, while in the first scheme the mixing occurs at a later stage. This, of course, leads to different yields of the products in the systems. If the reaction is isothermal and of an order greater than unity, a higher conversion will be attained in the first arrangement of apparatus. According to what has been said above, the plug flow reactor *1* corresponds to a higher degree of segregation than the backmix flow reactor *2* ($I_1 > I_2$).

On the basis of these considerations a different treatment of the effect of the level of mixing is also possible. Imagine a reactor with complete segregation, consisting of a long tube in which there is a piston-type stream or ideal plug flow, with a large number of closely packed lateral outlets (Fig. 5*a*). The stream flowing through these lateral outlets is controlled in such a way that the total distribution of residence times in the system is equal to the given distribution which is being investigated. It is assumed that the volume of the lateral outlets is insignificant. A very short section along the length of the tube may be regarded as a point in this system. Clearly the distribution of the ages at each point is extremely narrow and there is no mixing in the system, except for the mixing in the common outlet. Thus the mixing of molecules with different ages is achieved as late as possible, i.e. at point *A* (Fig. 5*a*).

A second imaginary flow system, with maximum mixing, can be obtained, by simple flow reversal, from the first flow system which is completely segregated. We then have many inlets and one outlet (Fig. 5*b*). It is assumed that mixing in the radial direction is ideal and that the flowing liquid is scattered immediately throughout the length of the tube. As soon as it enters the system, each molecule mixes with other molecules which will leave the system simultaneously. Thus mixing of the molecules occurs as soon as possible. This state is defined as the state of "maximum mixedness" — it is the opposite of the concept of total segregation[8].

Summarising the above findings, we arrive at the following most important conclusion: for a complete analysis of the operation of a chemical reactor, it is necessary to know (1) the reaction kinetics, (2) the response function of the system or the residence time distribution curve, (3) the properties of the system, i.e. the presence of macro- and micro-systems, and (4) whether mixing takes place during early or late stages.

In terms of classical kinetics, chemical reactions are considered at a microscopic level and consequently systems to which such kinetics are applied are microsystems.

The following conclusions may be made on the basis of the work of Danckwerts[7] and Zwietering[8]: (1) allowance for the degree of segregation and maximum mixedness is important only in homogeneous systems, since heterogeneous systems are always completely segregated, i.e. are always in a macrostate; (2) the degree of segregation and maximum mixedness must be taken into account only in stirred-flow tank reactors, since the streams in reactors operating on the total plug flow principle are always completely segregated; (3) in first-order reactions in homogeneous systems in stirred-flow tank reactors the conversion is independent of the level of mixing; the reaction rate is higher for the completely segregated state in reactions of an order greater than unity and lower in reactions of an order smaller than unity; (4) a plug flow reactor always

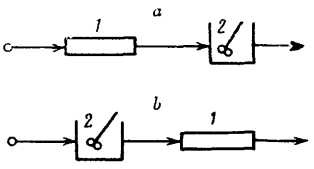


Fig. 4. Effect of the positioning of reactor models on the mixing level:
1) ideal plug flow; 2) ideal backmix flow.

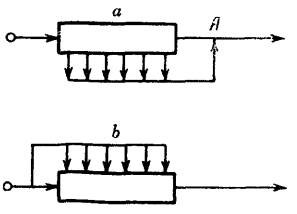


Fig. 5. Mixing in later (*a*) and earlier (*b*) stages.

gives a higher conversion than backmix flow reactors, both at the level of minimum and maximum segregation.

As mentioned above, to estimate the degree of non-uniformity of the distribution of the medium particles and hence the concentrations of the reactants in reactors, the corresponding distribution function is found by a statistical treatment of the experimental data on the variation of the concentration at the outlet from the reactor as a result of perturbations at the inlet, i.e. a cybernetic method is used to analyse the transmission of the signal through the test object.

Usually in the analysis of the distribution function for concentrations in reactors three types of perturbation (or, correspondingly, three types of input signal), differing in the mode of introduction of the tracer at the inlet, are used: step perturbation (step signal), pulse input signal (delta-function), and sinusoidal perturbation (frequency response) (Fig. 6).

At the outlet from the reactor the corresponding output signal (the time variation of tracer concentration at the outlet), whose form depends on the hydrodynamic conditions of the streams in the reactor, is obtained. The time parameter can be conveniently represented in the dimensionless form $\theta = \tau/\overline{\tau} = V_s\tau/V_r$, where τ is time in general and $\overline{\tau}$ the residence time of the tracer in the reactor, equal to the ratio of the volume of the reactor V_r filled with liquid to the volume of liquid V_s flowing in 1 s.

Step perturbation — F curve. In step perturbation the concentration of the tracer at the inlet reaches abruptly a constant value c_0. The distribution of the concentrations c at the inlet is then obtained in the form of the so-called F-curve, ranging from zero to $c/c_0 = 1$ (Fig. 6*a*).

Delta-function — C curve. In the case of pulse tracer injection (delta-function) the so-called C curve, shown in Fig. 6*b*, is obtained at the outlet.

Sinusoidal perturbation (frequency response). When the rate of injection of the tracer is varied harmonically, a sinusoidal curve, with a modified amplitude and phase angle, is obtained at the outlet (Fig. 6*c*).

The statistical distribution function for the tracer in the case of pulse perturbation can be written in the form (C curve)

$$C = \int_0^\infty \tau C(\tau)\, d\tau. \qquad (19)$$

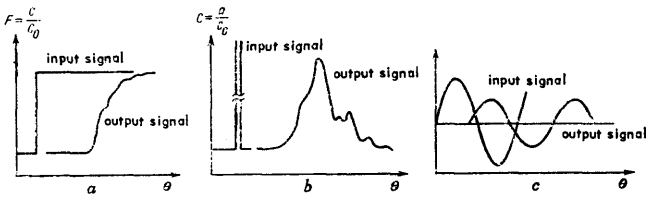


Fig. 6. The types of perturbation (input and output signals) used in the determination of the type of reactor model:
a) stepwise perturbation (F curve); *b*) delta-function (C curve);
c) frequency-response curves.

The residence time distribution function $C(\tau)$ characterises the fraction of the substance (tracer) in the exit stream which remained in the system for a time smaller than τ. The average residence time $\overline{\tau}$ is determined from the relation

$$\overline{\tau} = \frac{\int_0^\infty \tau C(\tau)\, d\tau}{\int_0^\infty C(\tau)\, d\tau} \simeq \frac{\Sigma \tau c}{\Sigma c}. \qquad (20)$$

The distribution function $C(\tau)$ is put in the form

$$C(\tau) = \frac{1}{\tau}\frac{c}{c_0} = \frac{c_0}{\Sigma c\, \Delta\tau}\ (s^{-1}), \qquad (21)$$

where $\Delta\tau$ is the sampling interval.

The dimensionless residence time θ is

$$\theta = \frac{\tau}{\overline{\tau}}.$$

When the average residence time is known, the C curve may be characterised by the equation

$$C = \frac{c}{c_0} = \overline{\tau} C(\tau). \qquad (22)$$

The variance or scatter of the quantity under consideration about the mean (for a continuous distribution), for a finite number of equidistant points (equal sampling intervals), is defined by the formula

$$\sigma^2 = \frac{\Sigma x_i^2 f(x_i)}{\Sigma f(x_i)} - \left[\frac{\Sigma x_i f x_i}{\Sigma f(x_i)}\right]^2. \qquad (23)$$

Thus when the variance is expressed in units of time, i.e. σ_τ^2 has the dimensions (seconds)^2, we have

$$\Sigma f(x_i) = \Sigma c_i;\ \Sigma x_i f(x_i) = \Sigma \tau_i c_i;\ \Sigma x_i^2 f(x_i) = \Sigma \tau_i^2 c_i;$$
$$\sigma_\tau^2 = \Sigma \tau^2 C(\tau)\Delta\tau - (\overline{\tau})^2.$$

The following expression holds for the variance in dimensionless units:

$$\sigma^2 = \frac{\sigma_\tau^2}{(\overline{\tau})^2} \qquad (23a)$$

or for the C distribution of the dimensionless time θ we have

$$\sigma^2 = \frac{\Sigma \theta^2 C}{\Sigma C} - 1 = \Sigma \theta^2 C \Delta\theta - 1. \qquad (23b)$$

The relation between the distribution functions for step and pulse perturbation is given by

$$C = \frac{dF}{d\theta};\quad F = \int_0^\theta C\, d\theta.$$

Since $C(\tau)d\tau$ characterises the fraction of the substance in the exit stream with the ages τ and $\tau + d\tau$, on multiplying this quantity by the concentration c_A of the reactant remaining in the element of stream with the age $\tau + d\tau$, we can determine the average concentration $\overline{c}_A$ of the unreacted reactant leaving a real reactor:

$$\overline{c}_A = \int_{\tau=0}^{\tau=\infty} c_A C(\tau)\, d\tau. \qquad (24)$$

Eqn. (24) is valid only for linear processes in which the output signal is directly proportional to the input signal and which therefore have the property of additivity. Bearing in mind that for first-order reactions the concentrations are related by the expression

$$c_A = c_{A_0} e^{-k\tau}$$

we can write, in conformity with Eqn. (24),

$$\bar{c}_A = c_{A_0} \int_0^\infty e^{-k\tau} C(\tau)\, d\tau. \quad (25)$$

Thus if information is available about the kinetics of the chemical reaction, we can determine by Eqn. (25) the conversion in a non-ideal reactor from the distribution curve $C(\tau)$ obtained experimentally for the given type of reactor.

Frequency response. The frequency response is obtained when the variation of the amount of tracer added is periodic (Fig. 6) at a definite frequency; the variation of tracer concentration at the inlet and outlet is then characterised by sinusoidal curves mutually displaced in amplitude and phase. The use of the method of frequency response for the analysis of reactors has been described by Kramers and Alberda [14] and has been developed by Mayer and Rippel [15]. Frequency analysis permits the replacement of time functions with the aid of the Laplace operator method. The Laplace operator is defined by the expression

$$F(p) = \int_0^\infty e^{-p\tau} f(\tau)\, d\tau. \quad (26)$$

In this method the time function $f(\tau)$ describing the behaviour of the reactor is replaced by the so-called transfer function $F(p)$. The latter is the ratio of the output function $F_{outp}(p)$ transformed by the Laplace method to the Laplace input function $F_{inp}(p)$:

$$F(p) = \frac{F_{outp}(p)}{F_{inp}(p)}. \quad (27)$$

If the transfer function is set up over a wide range of frequencies, it is possible to obtain a frequency response diagram which is then compared with the known frequency response diagram for ideal reactor models. Table 1 presents typical transfer functions for ideal reaction models and first-order reactions. By combining different models, it is possible to estimate the transfer function for a real reactor.

Consider an ideal backmix flow reactor in which a first-order reaction takes place. The following notation is introduced: V_s is the space velocity, c_{inp} the concentration of the reactant at the inlet, c_{outp} the concentration of the reactant at the outlet, k the reaction rate constant, and V_r the volume of the reactor. The material balance equation can be written in the form

$$V_s c_{inp} - V_s c_{outp} - k c_{outp} V_r = V_r \frac{dc_{outp}}{d\tau}. \quad (28)$$

After Laplace transformation, we have the equation

$$V_s c_{inp}(p) - V_s c_{outp}(p) - k c_{outp}(p) V_r = V_r c_{outp}(p)\, p, \quad (29)$$

where p is a Laplace operator.

The following expression for the concentrations of the reactant at the inlet to, and outlet from, the reactor can be obtained from Eqn. (29):

$$\frac{c_{outp}(p)}{c_{inp}(p)} = \frac{\frac{V_s}{V_r}}{\left(\frac{V_s}{V_r} + k + p\right)}. \quad (30)$$

On introducing the time constant $V_r/V_s = T$, we obtain the equation

$$\frac{c_{outp}(p)}{c_{inp}(p)} = \frac{1}{T\left(\frac{1}{T} + k + p\right)} \quad (31)$$

or

$$\frac{c_{outp}(p)}{c_{inp}(p)} \frac{1}{Tk + Tk + 1}. \quad (32)$$

The relation obtained describes a state which varies with time, i.e. a non-steady state. Since usually c_{outp}/c_{inp} is measured in the steady state where p is close to zero, Eqn. (32) can be reduced to the form

$$\frac{c_{outp}(0)}{c_{inp}(0)} = \frac{1}{Tk + 1}. \quad (33)$$

When Eqn. (33) is compared with the transfer function for the total backmix flow reactor (see Table 1), it is seen that the equation for first-order reaction kinetics in the steady state can be obtained from the transfer function on replacing p by the rate constant k. This opens up the possibility of assessing the process kinetics from the frequency response.

Two models based on the ideal reactor concept are used to analyse the operation of real reactors with non-linear systems. These models are the plug flow model with longitudinal or radial mixing (dispersion model) and the model with total mixing in individual tanks joined together in series, but without mixing of the contents of the different tanks (the tanks-in-series model).

TABLE 1. Typical transfer functions for ideal reactor models with first-order reactions.

Type of reactor	Transfer function	Remarks
Ideal backmix flow	$\frac{1}{T_1 p + 1}$	$T_1 = V_r/V_s$; V_r is the reactor volume and V_s the space velocity of the liquid
Ideal plug flow	e^{-pT_d}	$T_d = L/w$ is the transport lag, L the reactor length, and w the linear flow rate of the liquid
N ideal backmix flow reactors of equal volume in series (staged reactors)	$\frac{1}{(T_1 p + 1)^n}$;	
N ideal backmix flow reactors of unequal volume in series	$\frac{1}{(T_1 p + 1)(T_2 p + 1) \ldots (T_n p + 1)}$;	$T_1 = V_{r_1}/V_s$ $T_n = V_{r_n}/V_s$
Ideal plug flow and ideal backmix flow reactors in series	$\frac{e^{-pT_d}}{T_1 p + 1}$	

2. The Dispersion Model

As stated above, this model is based on the plug flow model with longitudinal and radial mixing. The coefficient of longitudinal or radial mixing D_L is analogous to the molecular diffusion coefficient in Fick's diffusion equation:

$$\frac{\partial c}{\partial \tau} = D_L \frac{\partial^2 c}{\partial l^2}. \quad (34)$$

In the theory of mass transport [16] the coefficient D_L is also called the coefficient of turbulent diffusion or of eddy transport, which describes its physical nature. For this reason, the model can also be called the *eddy model*.

The equation for the transport of the substance at a macroscopic level in a steady stream with allowance for

longitudinal mixing and chemical reaction takes the following form on the basis of the law of the conservation of matter:

$$w\frac{dc_A}{dl}-D_L\frac{\partial^2 C_A}{\partial l^2}+kc_A^n=0. \quad (35)$$

Eqn. (35) is normally used in a dimensionless form. For this purpose, we put $z = l/L$ and $\tau = L/w = V_r/V_s$, where L is the length of the reactor, w the linear flow rate across the total cross-section, V_r the reactor volume, and V_s the space velocity of the stream. On multiplying all the terms of Eqn. (35) by τ, we obtain

$$\frac{dc_A}{dz}=\frac{D_L}{wL}\frac{\partial^2 c_A}{\partial z^2}+k\tau c_A^n=0. \quad (36)$$

Introducing the conversion $x_A = (c_{A_0} - c_A)/c_{A_0}$, we obtain

$$-\frac{dx_A}{dz}+\frac{D_L}{wL}\frac{\partial^2 x_A}{\partial z^2}+k\tau c_{A_0}^{n-1}(1-x_A)^n=0. \quad (37)$$

In order to solve the above equation, it is necessary to know the value of the coefficient D_L, which is determined independently or from the experimental concentration distribution curve with respect to time, considered above for homogeneous and heterogeneous systems.

Usually the coefficient of longitudinal or radial mixing is determined in the dimensionless form D_L/wL, as in Eqn. (37), which is the reciprocal of the Peclet number $Pe = wL/D_L$. The choice of the linear dimension L, which is the determining dimension, is important. The dimensionless parameter D_L/wL varies from zero for an ideal plug flow stream to 1 for a total backmix flow stream.

Homogeneous systems. The distribution curves examined above, together with the values of the parameter D_L/wL, make it possible to determine the real reactor model, however much it may differ from ideal reactor models.

Fig. 7 shows C and F curves for a closed vessel corresponding to different values of the dimensionless parameter D_L/wL, in which the determining dimension L has been assumed to be the distance from the stream inlet to the stream outlet in the closed vessel. Levenspiel and Smith [17] and also Van der Laan [18] found from the C curve the relations between the variance σ^2 and the dimensionless parameter D_L/wL. For low deviations from ideal plug flow, which often obtain in tubular reactors, the C curves approximate closely to the normal Gaussian distribution and the relation between the variance and D_L/wL is represented by the equation

$$\sigma^2 = 2\frac{D_L}{wL}. \quad (38)$$

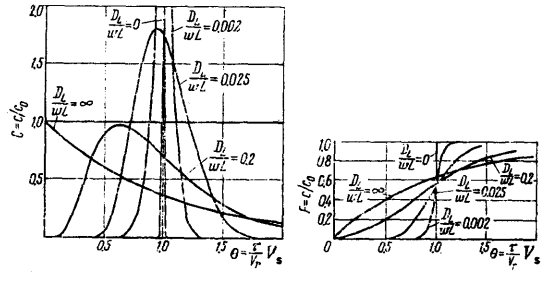


Fig. 7. Variation of output curves (C and F) with D_L/wL and θ.

When $D_L/wL < 0.01$, the maximum error associated with the use of Eqn. (38) is less than $5(D_L/wL)$, i.e. 5% when $D_L/wL = 0.01$ or 0.5% when $D_L/wL = 0.001$.

Table 2 presents different ways of using the dispersion models in homogeneous reactions under isothermal conditions [19].

Heterogeneous systems. In view of the importance of heterogeneous gas–solid systems for the analysis and calculation of the parameters of contact-catalytic processes, a large number of studies have been made [14,34-40] on the quantitative relation between the Peclet number for longitudinal ($Pe_L = d_p w/D_L$) and radial ($Pe_R = d_p w/D_R$) mixing and the Reynolds number Re in such systems. The particle diameter d_p is used as the determining dimension in the Peclet and Reynolds numbers, and the linear velocity of the liquid (gas) w is referred to the total cross-section of the apparatus. The results of these investigations are represented schematically in Fig. 8.

Fig. 8 shows that under turbulent conditions in gases and liquids the radial number Pe_R for mass transport is close to 12 (curve A), which agrees with Baron's theoretical calculations [41]. The Peclet number for longitudinal mixing in gases is approximately 2, which is also consistent with theoretical calculations [34,41], but differs from the experimental values for liquids. At low Re numbers, the "radial" and "longitudinal" Peclet numbers deviate from 2 and 12. In this case molecular diffusion has a significant influence.

Solution of the general form of the equation for the dispersion model. Because of its non-linearity, Eqn. (37) can be solved for specified boundary conditions only by numerical methods using computers.

TABLE 2. Different modes of utilisation of dispersion models.

Reaction order	Type of reaction	Type of flow	Mode of diffusion [dispersion]	References
0		turbulent	longitudinal	7,20,21
1/6–1/2	irreversible	turbulent	longitudinal	20
1	irreversible	laminar	radial	22–27
1	irreversible	turbulent	longitudinal	21,26–31
1	irreversible	turbulent	radial	23, 24
1	consecutive	turbulent	radial	27
1	reversible	turbulent	longitudinal	32
2	irreversible	laminar	longitudinal	31
2	irreversible	laminar	radial	22, 26
3	irreversible	turbulent	longitudinal	20, 30
	irreversible	turbulent	longitudinal	33

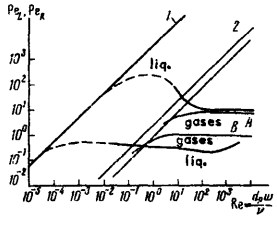


Fig. 8. Variation of the longitudinal (Pe_L) and radial (Pe_R) Peclet numbers with the Reynolds number Re:
1) molecular diffusion of liquids; 2) molecular diffusion of gases; A) radial diffusion; B) longitudinal diffusion.

The analytical solution of Eqn. (37) has been achieved only for first-order reactions. The following expression was obtained:

$$\frac{c_A}{c_{A_0}} = 1 - x_A = \frac{4a \exp\left(\frac{1}{2}\frac{wL}{D_L}\right)}{(1+a)^2 \exp\left(\frac{a}{2}\frac{wL}{D_L}\right) - (1-a)^2 \exp\left(-\frac{a}{2}\frac{wL}{D_L}\right)}, \quad (39)$$

where

$$a = \sqrt{1 + 4k\tau\left(\frac{D_L}{wL}\right)}.$$

The numerical solution of Eqn. (37) for first- and second-order reactions was achieved by Levenspiel and Bischoff[30] and by Fan and Bailie[28]. Levenspiel and Bischoff presented their solution in the form of graphs for different values of Pe_L, in which the ratio of the real reactor volume (taking into account longitudinal mixing) to the ideal plug flow reactor volume is plotted against the fraction of the unreacted reactant $c_A/c_{A_0} = 1 - x_A$. They concluded that for low conversions longitudinal mixing does not have much effect and the difference in the volumes of the ideal and real reactors is insignificant. It should be borne in mind that the dispersion model yields reliable results for comparatively small deviations from the ideal plug flow model and therefore the graphs described above can be used only for relatively low values of the parameter D_L/wL.

Effect of radial mixing. The effect of radial mixing is shown when the ratios of the tube diameter to particle diameter are low. Radial mixing is significantly influenced by the radial temperature profile, which leads to non-uniformity in conversion. A logical consequence of the radial gradient is a high rate of heat flow to and from the walls of the reactor. In principle, radial transport is an entirely desirable phenomenon for the elimination of hot spots along the reactor axis. The rate of radial diffusion may be increased by choosing a suitable ratio of tube diameter to particle diameter and a suitable temperature of the walls of the cooled reactor.

3. The Tanks-in-Series Model

The tanks-in-series model is based on the concept of the subdivision of the apparatus (reactor) into separate tanks. Within each tank ideal mixing takes place but there is no mixing between different tanks.

The relation between the C curve distribution and the number of tanks N is defined by the expression

$$C = \frac{c}{c_0} = \frac{N\theta^{N-1}}{(N-1)!} e^{-N\theta}, \quad (40)$$

where

$$\theta = \frac{\tau}{V_r/V_s}.$$

The relation between the number of tanks N and the variance σ^2 is

$$\sigma^2 = \frac{1}{N} = 2\frac{D_L}{wL} - 2\left(\frac{D_L}{wL}\right)^2\left(1 - e^{-\frac{wL}{D_L}}\right) \quad (41)$$

or Eqn. (38) can be used with adequate accuracy for practical calculations:

$$\sigma^2 = \frac{2}{N} = 2\frac{D_L}{wL}.$$

Assuming total mixing of the gas within the free volume of a monolayer of catalyst particles in the direction of the stream, the number of total backmix flow tanks is evidently L/d_p. The relation between the number of such tanks N and longitudinal macrodiffusion D_L, the length of the catalyst bed, and the gas flow rate w is

$$N = \frac{Lw}{2D_L}. \quad (42)$$

When $N = L/d_p$, then $wd_p/D_L = 2$ and the reactor operates as staged total backmix flow tanks.

Fig. 9, which has been constructed on the basis of Carberry's data[40] for a first-order reaction under isothermal conditions, shows the variation of the ratio of the conversion in a stationary bed x_{mix} and the conversion x_{plug} in a reactor without mixing (total plug flow reactor) with the product of the first-order reaction rate constant k and the duration of contact τ. Similar relations have been obtained for non-isothermal and non-adiabatic conditions[42,43].

The relation between the Pe_L number for a plug flow reactor and the number of tanks (or the number of staged reactors) is shown clearly in Fig. 10, based on the data of Trambouze[44].

4. Mixed Models

Apart from the plug and backmix flow streams examined above, additional phenomena occur in real reactors, such as stream circulation, their by-pass flow, cross-over streams, and stagnant zones. The model of the streams in a real reactor is then set up by means of different combinations of ideal backmix flow and plug flow models, stagnant zone models (concentration assumed to be constant),

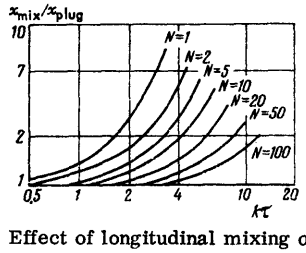


Fig. 9. Effect of longitudinal mixing on first-order processes.

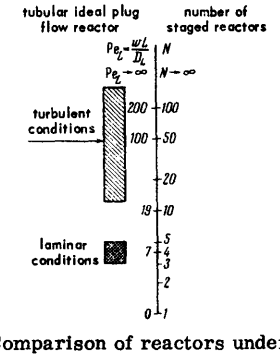


Fig. 10. Comparison of reactors under different hydrodynamic conditions.

etc. Subsequently the output concentration curves for a real reactor are compared with curves constructed on the basis of the proposed combination of models [5]. Table 1, quoted above, is very useful for this purpose.

The simplest mixed reactor models were examined in Levenspiel's monograph [12] and treated systematically by Wen and Chung [19]. The stagnant zone method of calculation, which gives better results than Levenspiel's method, has been described recently [45].

IV. EFFECT OF THERMAL PARAMETERS ON CHEMICAL PROCESSES

The distribution of temperatures in a stream (along the axis t and for radius R) in the presence of a chemical reaction can be represented in the following form, in conformity with the law of conservation of energy:

$$\frac{\partial t}{\partial \tau} = -w\frac{\partial t}{\partial l} + D_{Lq}\frac{\partial^2 t}{\partial l^2} + \frac{D_{Rq}}{R\partial R}\left(R\frac{\partial t}{\partial R}\right) + \frac{w_r(\pm \Delta H)}{c_p\gamma},$$

where $\partial t/\partial\tau$ is the rate of change of temperature with time. If in the system under consideration the heat of chemical reaction evolved is entirely consumed in changing the heat content of the system, the reactor used under such conditions is referred to as an adiabatic reactor. The temperature of the reaction mixture, defined by the ratio $T_a = (\pm\Delta H)c_{A_0}/\gamma c_p$, is then called an adiabatic temperature.

Depending on the model, the following heat balance equations hold for adiabatic reactors:

for a backmix flow reactor

$$V_s\gamma c_p(t_e - t_i) = V_s(c_e - c_i)(\pm\Delta H), \quad (43)$$

for a plug flow reactor

$$V_s\gamma c_p dt = w_r(\pm\Delta H)\,dV_r. \quad (44)$$

The following heat balance equations hold for a polytropic reactor, depending on its model:

for a backmix flow reactor

$$V_s\gamma c_p(t_e - t_i) = V_s(c_e - c_i)(\pm\Delta H) - \alpha F(t_e - t_x), \quad (45)$$

for a plug flow reactor

$$V_s\gamma c_p dt = w_r f(\pm\Delta H)dz - \alpha F'(t - t_x)dz = V_s(\pm\Delta H)dc - \alpha F'(t - t_x)dz. \quad (46)$$

The following notation is used in the above equations: w_r is the rate of change of concentration due to the chemical reaction, w the linear flow rate, V_s the space velocity of the reaction mass, D_{Lq} and D_{Rq} are the coefficient of longitudinal and radial heat transport, γ is the specific gravity, c_p the specific heat at constant pressure, ΔH the heat of reaction (the plus sign corresponds to an endothermic reaction and the minus sign to an exothermic reaction), t_i and t_e are the initial and final temperatures of the reaction mass, c_i and c_e the initial and final concentrations of the reactants, α is the coefficient of heat transfer from the reaction mass to the cooling agent, t_x the temperature of the cooling agent, F the heat exchange surface area, F' the heat exchange surface area referred to unit length, and f the cross-sectional area of the stream in the reactor.

Isothermal reactors are relatively infrequently used in large-scale processes because of the high cost of the heat-exchange equipment. Therefore adiabatic or polytropic industrial reactors are usually designed.

Cholette and Blanchet [46] made a theoretical comparison of the conversion in an adiabatic plug flow reactor with that in a backmix flow reactor (for a microstate). The comparison yielded the same results for both endothermic and isothermal reactions, i.e. the plug flow reactor proved to be superior to the backmix flow reactor. For exothermic reactions at low conversions, the backmix flow reactor proved to be more convenient than the plug flow reactor, but at high conversions the opposite was true.

The above estimate of the average reaction rates provides an explanation of these findings. The rate of endothermic reactions decreases with the conversion as a result of the consumption of the reactants and the decrease of the temperature of the system. Since the average rate of reaction in the plug flow reactor, where it assumes a value which is the average of the maximum rate at the inlet and the minimum rate at the outlet, is always higher than the average rate in the backmix flow reactor, it follows that in the presence of heat exchange too the plug flow reactor is always preferable to the backmix flow reactor.

The rates of most exothermic processes initially increase with the conversion, as a result of the increasing temperature of the system, but at high conversions they fall due to the consumption of the reactants. Under conditions of increasing rate, the average reaction rate in the backmix flow reactor is always higher than in the plug flow reactor. However, after the attainment of a certain conversion, somewhat higher than that corresponding to the maximum rate, the average rates in both reactor models become identical and at higher conversions the plug flow reactor again becomes more advantageous.

The variation of the conversion with the residence time in plug flow and backmix flow reactor models (at two levels) is shown in Fig. 11 for endothermic reactions and in Fig. 12 for exothermic reactions. In the graphical construction of the conversion profiles, use was made of the temperature variation of the reaction rate based on the Arrhenius equation, and temperature was eliminated by setting up the heat balance for an adiabatic reactor (with subsequent analytical or numerical solution), the following conditions being assumed: $ER/T_0 = 40$ and $T_a/T_0 = 0.1$, where $T_a = (\pm\Delta H)c_{A_0}/\gamma c_p$ is the adiabatic temperature and T_0 the initial temperature.

Comparison of the segregated state with mixing at the molecular level for endothermic reactions (Fig. 11) shows that the highest conversion is attained for reactions of any order in the segregated state. The difference between this result and the result considered for isothermal conditions,

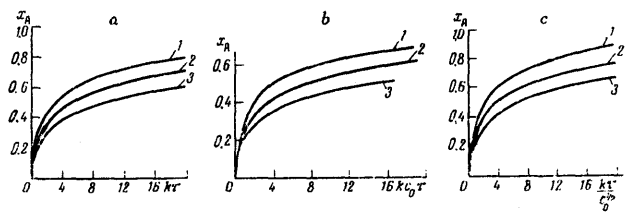


Fig. 11. Dependence of the conversion on the reactor model and the mixing level for endothermic reactions of different orders: *a*) first-order reactions; *b*) second-order reactions; *c*) reactions of order 1/2;
1) plug flow reactor; 2) backmix flow reactor (macromixing); 3) backmix flow reactor (micromixing).

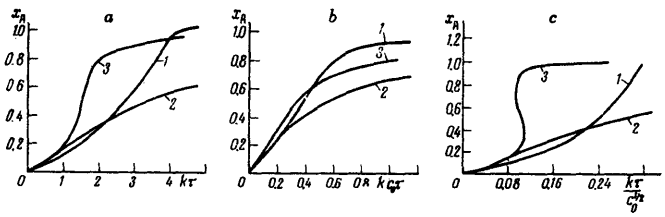


Fig. 12. Dependence of the conversion on the reactor model and the mixing level for exothermic reactions of different orders: *a*) first-order reactions; *b*) second-order reactions; *c*) reactions of order 1/2:
1) plug flow reactor; 2) backmix flow reactor (macromixing); 3) backmix flow reactor (micromixing).

where the order of the reaction has a significant influence, is due to the mode of variation of the reaction rate. In an endothermic system the rate decreases with increasing conversion, both due to the disappearance of the reactants and the decrease of the temperature of the system. In the systems examined above the temperature effect was greater than the compensation due to the order of the reaction.

Comparison of the segregated state with mixing at a molecular level for exothermic reactions (Fig. 12) leads to the opposite conclusion — the highest conversion corresponds to mixing at a molecular level. This is because in exothermic systems the initial rate increases with conversion due to the increasing temperature of the system.

Combinations of reactor models have been considered by Cholette and Blanchet[46]. It was shown that for exothermic reactions a combination of plug flow and backmix flow (at a molecular level) reactors is sometimes more satisfactory than the individual reactor models. Douglas notes[47] that some of Spencer's calculations[48], based on the dispersion model, have shown that the optimum conversion is attained at a certain finite non-zero value of the mixing parameter, i.e. for a hypothetical case intermediate between the plug flow and backmix flow reactor models. These findings can be explained by considering the variation of the average reaction rate in the two systems.

Denbigh[49] showed that the plug flow reactor is always preferable in cases where the rate of reaction decreases with increasing conversion. On the other hand, the backmix flow reactor is more advantageous when the rate increases during the reaction. Therefore, for exothermic reactions whose rate passes through a maximum as the conversion increases, the optimum model is the backmix flow reactor under conditions of increasing rate and the plug flow reactor under conditions of falling rate.

Aris[50] made a quantitative estimate based on the above postulates and showed that, for a reaction of the type A → products,

$$w_r = kc_{A_0}(1-x_A) = c_0^n\left(A\exp\frac{-E/RT_0}{1+\frac{T_a}{T_0}x_A}\right)(1-x_A)^n; \qquad (47)$$

the condition corresponding to the maximum reaction rate w_r is $\partial w_r/\partial x_A = 0$ and the required conversion x at the outlet may be obtained by a combination of backmix flow reactors. The following equation then holds:

$$n\left(1+\frac{T_a}{T_0}x_A\right)^2 = (1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}. \qquad (48)$$

It has been shown that the best model for reversible gas-phase reactions may be obtained by setting up a decreasing temperature profile[51] which can be attained by by-passing a cold feed. Aris[51] examined by-pass schemes with two and three adiabatic reactors and also other optimum schemes.

A comparative assessment of reactor models can be conveniently made by comparing the slopes $dx_A/d\tau$ of $x_A-\tau$ curves, i.e. by differentiating the material balance equations for reactors under different heat-exchange conditions[47]. On the basis of Eqn. (47), we have for the plug flow reactor

$$c_{A_0}^{1-n}\frac{dx_A}{d\tau} = k(1-x_A)^n. \qquad (49)$$

After appropriate substitutions, the material balance equation for the backmix flow reactor yields the expression

$$c_{A_0}^{1-n}\frac{dx_A}{d\tau} = k(1-x_A)^n\left[\frac{1-x_A}{1+(n-1)x_A - x_A(1-x_A)\frac{1}{k}\frac{dk}{dx_A}}\right]. \qquad (50)$$

Comparison of Eqns. (49) and (50) shows that the slope of the $x_A-\tau$ curve for the backmix flow reactor differs from the slope of the curve for the plug flow reactor by the factor

$$\left[\frac{1-x_A}{1+(n-1)x_A - x_A(1-x_A)\frac{1}{k}\frac{dk}{dx_A}}\right]. \qquad (51)$$

Under isothermal conditions we have

$$\frac{dk}{dx_A} = 0,$$

and the factor (51) reduces to the form

$$\left[\frac{1-x_A}{1+(n-1)x_A}\right]. \qquad (52)$$

Since the above factor is always less than unity, the slope of the curves for the total backmix flow reactor is always smaller than the slope for the plug flow reactor and therefore under isothermal conditions the plug flow reactor is always preferable to the backmix flow reactor.

Under endothermic conditions we have

$$\frac{dk}{dx_A} = \frac{d}{dx_A}\left[A\exp\left(\frac{-E/R}{T_0-T_ax_A}\right)\right] = -\frac{k\frac{E}{RT_0}\frac{T_a}{T_0}}{\left(1-\frac{T_a}{T_0}\right)^2}. \qquad (53)$$

On substituting Eqn. (53) in Eqn. (51) and assuming that the factor (51) is always less than unity, i.e. that the slope of the $x-\tau$ curves for the backmix flow reactor is always smaller than the slope of the curves for the plug flow reactor, we obtain the inequality

$$-n\left(1-\frac{T_a}{T_0}x_A\right)^2 < (1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}. \qquad (54)$$

Since the left-hand side of this expression is always negative and the right-hand side is always positive, the factor (51) is indeed smaller than unity. Therefore for endothermic reactions a plug flow reactor will always give a higher conversion per unit volume.

For exothermic reactions, we have the equation

$$\frac{dk}{dx_A} = \frac{d}{dx_A}\left[A\exp\left(\frac{-E/R}{T_0+T_ax_A}\right)\right] = \frac{k\frac{E}{RT_0}\frac{T_a}{T_0}}{\left(1+\frac{T_a}{T_0}x_A\right)^2}. \qquad (55)$$

It follows from Fig. 12 that the slopes of $x-\tau$ curves for the backmix flow reactor are higher than the slopes of the

curves for the plug flow reactor at low conversions, are equal at a certain intermediate conversion, and lower at high conversions. Therefore on substituting Eqn. (55) in expression (51), we should obtain a factor greater than unity at low values of x and smaller than unity at high values of x:

$$\frac{(1-x_A)\left(1+\frac{T_a}{T_0}x_A\right)^2}{[1+(n-1)x_A]\left(1+\frac{T_a}{T_0}x_A\right)-x_A(1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}} \begin{matrix} > 1 \text{ small } x \\ = 1 \text{ intermediate } x \\ < 1 \text{ large } x \end{matrix} \quad (56)$$

or

$$n\left(1+\frac{T_a}{T_0}x_A\right)^2 \lessgtr (1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}. \quad (57)$$

It is evident from formula (57) that at high conversions the right-hand side approaches zero (when x_A tends to unity). At a very low conversion ($x \simeq 0$) the following inequality can be obtained from formula (57):

$$n < \frac{E}{RT_0}\frac{T_a}{T_0}. \quad (58)$$

The inequality (58) is valid for the majority of exothermic systems. It is noteworthy that, if this relation does not hold, the rate of reaction decreases with increasing conversion and the plug flow reactor is more advantageous than the backmix flow reactor.

To determine the optimum combination of reactor models, consider the graphical method based on the construction of a conversion profile [46,47,52]. On the basis of Fig. 12, characterising the conversion profile for individual reactor models, one constructs a conversion curve for exothermic reactions in the backmix flow reactor (Fig. 13, curve *1*) which gives the steepest possible curve. If a system comprising a combination of two reactor models (backmix flow–plug flow) is proposed, a second curve for the plug flow reactor must be constructed (curve *2*). The point A corresponding to the highest slope of the curve for the backmix flow reactor is selected. The line AB, parallel to the curve for the plug flow reactor along the section CD, is drawn from point A. The line AB characterises the conversion which obtains for the combination of the two reactors. However, this profile does not yield the optimum system, because evidently best conditions can be achieved if the system includes a larger backmix flow reactor and a smaller plug flow reactor. Similarly if the conditions of the backmix flow reactor correspond to those at point G and a profile is constructed for the combined system, better conditions can be attained in a system with a smaller backmix flow reactor. Therefore under the conditions at point

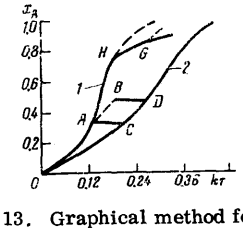


Fig. 13. Graphical method for the construction of combined reactor models:
1) backmix flow reactor (micromixing); 2) plug flow reactor.

H (the point corresponding to equal slopes of the curves) the optimum reactor combination is obtained.

Thus the following conclusions can be arrived at on the basis of the above considerations: the ideal plug flow reactor is always more advantageous for isothermal and endothermic conditions, while for exothermic conditions a combination of reactor systems is more suitable. The optimum temperature profile for complex reactions has been examined by Bilous and Amundson [53]. Slin'ko [54] calculated optimum temperature profiles for contact-catalytic reactors.

V. THERMAL STABILITY OF CHEMICAL REACTORS

The concept of the stability of systems was first formulated by Lyapunov [55]. A system is regarded as stable if after the removal of any perturbation it returns to the previous state. When thermal stability of chemical reactors is considered, perturbations can arise in the system in exothermic processes due to the different mode of heat supply and heat removal. The thermal stability of chemical reactors has a significant effect on the temperature and concentration profiles in the reactor and also provides information which can be used in the selection of the automatic reactor control system.

Assuming that the heat gained by the reactor is evolved in the chemical reaction, i.e.

$$dQ_{\text{infl}} = w_r \Delta H\, dV_r = k_0 e^{-E/RT} c_{A_0}^n (1-x_A)^n \Delta H\, dV_r \quad (59)$$

and the heat loss is determined by the heat content change in the system and by an external heat exchanger,

$$dQ_{\text{outfl}} = V_s \gamma c_p\, dt + \alpha F' (t - t_x)\, dz \quad (60)$$

it is readily seen that the relation between the heat gained and the temperature of the system is exponential, while that between the heat lost and the temperature of the system is linear, i.e. in an exothermic reaction the rate of heat gain is much faster than the rate of its loss and can result in an undesirable increase in the temperature of the system. This fact was pointed out at one time by Semenov [56] and Frank-Kamenetskii [57]. Under endothermic conditions, the problem of stability does not arise.

The necessary condition for the stability of the reactor with respect to heat is

$$\frac{dQ_{\text{outfl}}}{dT} \geqslant \frac{dQ_{\text{infl}}}{dT}. \quad (61)$$

It follows from the heat-exchange conditions in different reactor models examined earlier that the stability conditions also depend on the reactor model and the degree of conversion in the system.

A characteristic feature of the temperature profile of a tubular plug flow reactor with an external heat exchanger is that the reaction volume is proportional to the square of the diameter, while the surface area of the heat exchanger is proportional to the diameter. Therefore in tubes of large diameter the instability is more pronounced than in tubes of small diameter.

As the process proceeds in a plug flow reactor, the temperature initially rises fairly rapidly and the rate of heat loss also increases. The maximum temperature is attained at the point where the local rate of heat loss is equal to the rate of heat supply as a result of the reaction. With increasing conversion, the reaction rate falls, which leads to

a decrease of the temperature in the reaction zone, the temperature approaching that of the cooling agent. Only for a reaction of zero order, whose rate is independent of concentration, does the temperature in the reactor remain constant at the maximum value until the reaction is complete. It should be borne in mind that, with the exception of autocatalytic reactions and reactions with an induction period, the maximum reaction rate at a given temperature is the initial rate, i.e. the rate at the inlet to the reactor, where in fact there is a risk of a sharp rise of temperature.

The stability criteria can be found directly from the balance equations examined previously. According to Eqns. (10) and (49), the following expression is valid for an exothermic first-order reaction in an ideal backmix flow reactor of fixed volume:

$$x_A = k\tau(1-x_A). \tag{62}$$

The requirement for stability is[61] that the derivative of the left-hand side of Eqn. (62) with respect to x_A should be greater than the derivative of the right-hand side, representing the heat gain. Then, in conformity with Eqn. (55), we have the inequality

$$1 > -k\tau + \tau(1-x_A)\frac{k\frac{E}{RT_0}\frac{T_a}{T_0}}{\left(1+\frac{T_a}{T_0}x_A\right)^2}. \tag{63}$$

Using Eqn. (62), the product $k\tau$ can be eliminated from the last expression and the stability criterion is obtained in the form[47]

$$\frac{\left(1+\frac{T_a}{T_0}x_A\right)^2 - x_A(1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0}}{(1-x_A)\left(1+\frac{T_a}{T_0}x_A\right)^2} > 0. \tag{64}$$

We may note that when the stability condition is defined by the inequality (64), the inequality (57) becomes unambiguous.

If condition (64) is satisfied for all conversions, the so-called global stability obtains. The relations between the parameters E/R, T_a, and T_0 can then be found. For this purpose, it is necessary to know the values of x_A at which condition (64) is minimised.

Let

$$h = \left(1+\frac{T_a}{T_0}x_A\right)^2 - x_A(1-x_A)\frac{E}{RT_0}\frac{T_a}{T_0} > 0. \tag{65}$$

The value of x_A for which h is a minimum can be found from the condition $\partial h/\partial x_A = 0$:

$$x_{A_{min}} = \frac{\frac{E}{RT_0}-2}{2\left(\frac{T_a}{T_0}+\frac{E}{RT_0}\right)}. \tag{66}$$

On substituting Eqn. (66) in Eqn. (65), we obtain

$$h_{min} = \frac{\frac{E}{RT_0}\left[1+\frac{T_a}{T_0}\left(\left[1-\frac{1}{4}\frac{E}{RT_0}\right)\right]\right.}{\frac{T_a}{T_0}+\frac{E}{RT_0}}. \tag{67}$$

The stability of the ideal backmix flow reactor has been analysed by Van Heerden[58], who was the first to show that several stable states are possible. Bilous and Amundson[59] made a quantitative analysis of stability criteria on the basis of the equation for the non-steady state. Aris and Amundson[60] analysed the stability of the ideal backmix flow reactor without a regulator and also with a proportional regulator, which enhanced the stability. The results of the analysis were presented in the form of phase diagrams in terms of dimensionless concentration–temperature coordinates. The stability of the ideal plug flow reactor has also been analysed by Van Heerden[58].

The stability conditions for a semicontinuous reactor with a stirrer, taking into account the residence time of the reaction mass in the reactor, were formulated by Kafarov and Eremenko[61]. They also indicated scaling methods for reactors of different dimensions, with maintenance of stability conditions, which is very important in industrial practice.

Simchen[62] obtained a solution in the form of the transcendental equation $\exp(-E/RT) = a(T - T_w)$ (where a is a constant depending on the physical parameters of the system) for temperatures corresponding to the points of intersection of the heat gain and heat loss lines, taking into account the temperature of the reactor walls T_w.

The maximum permissible temperatures for a given conversion and selectivity in stirred reactors for parallel and consecutive reactions have been examined by Westerterp[63]. The practical difficulties encountered in the attempts to attain the required process temperature were demonstrated, using the synthesis of phthalic anhydride as an example. Liu Shean Lin and coworkers[64,65] analysed the stability of adiabatic and non-adiabatic reactors with a stationary catalyst bed. The mathematical model was reduced to an examination of the behaviour of the individual particles immersed in the gas stream, when the resistance to heat and mass transport is concentrated on the surface of the particles. An irreversible first-order reaction in the absence of longitudinal and radial gradients of gas flow rates was considered. The balance equations were solved numerically by the response curve method and a graphical interpretation of the solutions was given. The following findings were obtained for the adiabatic reactor. In the initial sections of the bed the stable state is attained relatively rapidly, compared with the output from the bed. At low temperatures the difference between the temperatures and concentrations in the gas and solid phases is almost negligible. These are kinetic conditions, since at low temperatures the chemical reaction is very slow. When the temperature of the particles is relatively high, the chemical reaction is accelerated and heat is rapidly evolved. The process becomes diffusion-dependent. A considerable difference between the concentrations and temperatures in the gas and solid phases then arises.

At a relatively low temperature of the gas at the inlet, the chemical reaction virtually does not take place via the bed and the concentration and temperature profiles are planar. On raising the gas temperature at the inlet, the conversion increases rapidly, becoming almost complete at a certain temperature (the temperature gradient in the bed is then almost zero). The higher is the concentration (partial pressure) of the component at the inlet to the bed the higher is the temperature of the exit gas and the chemical reaction is completed over a relatively short length of the bed. Different profiles are possible for the same temperature and concentration at the inlet and the system may be unstable, depending on the existence of local steady states and their multiplicity for individual particles.

If each particle along the axis of the bed had only one steady state, the reactor would be stable and there would be unique concentration and temperature profiles for all the initial temperatures and particle concentrations.

Due to the heat transmitted via its walls, in a non-adiabatic reactor there is instantaneous radial heat and mass transport in the reactor itself. The temperature within the bed can then be lower than the temperature of the inflowing gas and therefore under non-steady conditions the state of the particles may be different than in the adiabatic reactor. The temperature profile changes sharply as a result of slight change in the temperature of the gas at the inlet. The temperature and concentration profiles vary markedly with the coefficients of heat transfer from the particles in the bed to the gas and from the gas to the reactor walls. Furthermore, as in the adiabatic reactor, there is a possibility of the occurrence of non-unique temperature and concentration profiles, depending on the presence of a multiplicity of states for individual particles. The stability of the system is affected by the initial conditions, such as the initial temperature of the particles of the bed, the temperature of the inflowing gas, and the partial pressure of the reactant. These findings[64,65] agree with earlier investigations[66-68]. Barkelew analysed the stability of reactors with a stationary bed by introducing empirical dimensionless parameters[69].

The stability of contact-catalytic reactors was analysed in the widely recognised work of Boreskov[3], Slin'ko[54], Beskov[70], and others. In these studies the stability conditions were formulated, whereby it is possible to calculate the maximum permissible tube diameters in contact-catalytic apparatus for various synthetic processes. It has been shown that the contact-catalytic unit, consisting of two stable reactors, can have unstable states. The problems of the optimisation of the contact-catalytic apparatus for industrially important processes such as the oxidation of sulphur dioxide, ethylene, methanol, and others were also developed in these investigations.

Kafarov et al.[71] provided a mathematical foundation for the stability criterion. Approximate stability conditions were found[72] for a non-continuous ideal backmix flow reactor with regulation of the coolant temperature and the rate of reactant injection and also for the load period of a semi-continuous reactor with regulation of the coolant temperature. One of the possible ways of increasing the stability of the process in chemical reactors, consisting in setting up an automatic control system for the coolant temperature in the refrigerator and for the rate of injection of reactants as a function of the temperature of the reaction mass, was demonstrated.

Using Lyapunov's method, a number of investigators[60,73-75] analysed the stability of a reactor in the presence of non-continuous perturbations and various control systems. Hoftyzer and Zwietering[76] investigated the stability and control of the ethylene polymerisation process and established that, for certain versions of the set up, there are five possible solutions corresponding to stable states. The stability of chemical reactors for two-phase systems, taking into account the possibility of regulation, was investigated by Schmitz and Amundson[77]. Later Amundson and co-workers[78,79] developed mathematical methods for the analysis of the stability of tubular reactors.

VI. EFFECT OF DIFFUSION PARAMETERS ON CHEMICAL PROCESSES

Depending on the effect of *diffusion macrofactors*, chemical processes can be divided into (1) chemical processes under "kinetic" conditions, (2) chemical processes under diffusion-dependent conditions, and (3) chemical processes under mixed conditions.

A characteristic feature of chemical processes under kinetic conditions is that the rate of the chemical reaction itself is slowest, limiting the rate of the process as a whole, while the flow rates of the streams and their physical properties do not influence the process appreciably. In chemical processes under diffusion-dependent conditions the rate of diffusion of reactant to the reaction zone is rate-limiting and depends on the flow rates of the streams and their physical properties. A characteristic feature of processes occurring under mixed conditions is that the rates of chemical reaction and diffusion are comparable.

The possibility, in principle, of isolating the rate-limiting stage is based on the fact that in many cases a complex process consists of several consecutive stages. The slowest rate is rate-limiting. The methods available for the determination of the rate-limiting stage of the process, i.e. of determining whether diffusion-dependent or kinetic conditions predominate, are as follows[80].

1. Determination from the temperature coefficient of the overall rate of the process. If on changing the temperature by 10 deg the overall rate of the process changes by a factor of 2–3, then, as a rule, the chemical reaction itself is the rate-limiting stage. On the other hand, if a 10 deg temperature change entails a change in the rate of the process by a factor of less than two, mass exchange is the rate-limiting stage. In intermediate cases the reaction takes place under mixed diffusion-dependent and kinetic conditions.

2. Determination from the apparent order of the reaction. If the order is not unity, the rate-limiting stage is the chemical reaction. However, if the order is unity, the question of the rate-limiting stage remains open, since the mass exchange process is also directly proportional to the concentration.

3. Determination from the variation of the overall rate of the process with its hydrodynamic conditions. If the rate of the process is independent of the hydrodynamic conditions, the rate-limiting stage is either mass exchange or simultaneously mass exchange and the chemical reaction (i.e. the reaction takes place under mixed diffusion-dependent and kinetic conditions).

Under diffusion-dependent conditions the rate of the reaction, like the diffusion coefficient, varies relatively little with temperature but changes with the flow rate of the gas stream, like the Nusselt diffusion number[16], i.e. is proportional to the gas flow rate raised to the power of 0.4–0.5 for outside flow and to the power of 0.8 for turbulent motion in inside flow.

Under diffusion-dependent conditions the rate of reaction in no way depends on the concrete features of its chemical mechanism; the rates of a wide variety of reactions differ only because of differences in the diffusion coefficients of the reactants and in the case of reversible reactions because of differences in the equilibrium conditions. All the reactions under diffusion-dependent conditions are of first order with respect to the reactant concentration at a constant total pressure. The order of the reaction with respect to the total pressure differs from the order with respect to the concentration.

Diffusion-dependent conditions obtain at high reaction rates and low rates of diffusion, i.e. at high temperatures, high pressures, and low gas flow rates. On the other

hand, at low temperatures, low pressures, and high gas flow rates, kinetic conditions obtain. In the intermediate region mixed diffusion-dependent and kinetic conditions obtain, where the effect of both diffusion and reaction kinetics is significant. The effects of chemical reactions and diffusion can be taken into account quantitatively (using the additivity principle) and simultaneously only for linear systems, i.e. first-order reactions. The solution of non-linear problems usually reduces to finding a rate-limiting stage in the process.

Examination of the model of the contact-catalytic chemical process from the standpoint of transport phenomena shows that the process takes place simultaneously at microscopic and macroscopic levels. Axial and radial dispersion of heat and mass between the particles, transport of heat and mass between the phases, and transport within the particles take place. Much work has been done in recent years on the study and analysis of transport phenomena in contact--catalytic processes. Since these studies cannot be considered here, the reader is referred to two detailed reviews on this topic [40,81] and also to recent monographs [82,83].

The studies of chemical processes on free surfaces in gas–liquid, vapour–liquid, and liquid–liquid systems have been attracting increasing attention in recent years. The so-called "extractive" reactions, involving the addition of an immiscible solvent to a homogeneous system during chemical reaction in order to remove a side-product or the required product, have been finding increasing application in chemical industry. The chemical process and extraction are carried out continuously [84-87]. A similar principle is used in the application of absorption and fractionation [88]. The effect of mixing on the chemical reaction in liquid–liquid and gas–liquid systems, which is important under these conditions, has been studied by a number of investigators [89-93]. It has been shown that, in a reaction system with mixing, physical equilibrium between the phases may not be attained.

In the construction of mathematical models of chemical processes in two-phase systems, usually one of two possible models is adopted for each phase: the model with centralised parameters and the model with distributed parameters. The model with centralised parameters includes one independent variable, namely time. In models with distributed parameters the variation of variables with time and space is considered, which leads to partial differential equations. The mixing process in homogeneous systems can be described by the model with centralised parameters with an accuracy which is satisfactory for practical purposes. In heterogeneous systems the model with centralised parameters can be applied to the continuous phase and the model with distributed parameters to the disperse phase. In contact-catalytic processes with a solid phase, the catalyst may be regarded as a disperse phase. On the other hand, if the disperse phase is a liquid, the occurrence of internal circulation, coalescence, and redispersion permits the assumption of ideal mixing within the limits of each drop and therefore the model with centralised parameters may be applied to both phases.

However, in a disperse phase account must be taken of the scatter of the values of the dependent variables, i.e. of the presence of a definite distribution of the medium particles (drops) with respect to the residence time (the "age"). If, on the other hand, the drops coalesce and undergo redispersion at a very high rate, the distribution may be evened out. This is most likely for two liquid phases and less likely if the disperse phase is a gas. In practical calculations, it is usually assumed that there is no definite distribution in the disperse phase.

In the construction of mathematical models, one of the following schemes is adopted: (1) the rates of heat and mass transport between the phases are high and the rate of conversion is rate-determining or (2) the rates of transport at the interface are high and therefore the system is in physical equilibrium. According to the second scheme, mass transport is rate-determining, i.e. under these conditions the rate of reaction is so high that the course of the process as a whole is determined by the rate of transport of the reactants. The reactants and the reaction products in the reacting phase are in chemical equilibrium and their concentration in this phase is defined by an equilibrium constant. In intermediate cases the concentrations do not correspond to equilibrium relations and the temperatures of the phases are not the same, and therefore it is then necessary to take into account all the rates of the process.

Various combinations of the above models are possible in cases where the reactions take place at different rates in one or two phases. For example, the reaction may be so fast in one phase that the reaction components are in chemical equilibrium, and the overall rate of reaction is then determined by the conversion in the second phase. More complex situations can also arise in the presence of consecutive, parallel, and other complicated reactions. A number of problems of this kind have been examined in the work of Schmitz and Amundson [77] (quoted previously), who investigated the conditions of stability and control in reactors with stirred two-phase systems. A number of studies on the attainment of conditions corresponding to the occurrence of reactions on free surfaces in liquid-phase systems have been made by Abramzon and coworkers [94]. The studies on chemical reactors for gas–liquid systems have been reviewed by Teller [95].

The effect of circulation on chemical processes and calculations on circulation systems have been described in Nagiev's monograph [96]. Calculations on contact-catalytic processes taking into account circulation are quoted in Orochko's monograph [97] and in a number of later papers of Zinov'eva and Orochko [98]. They also consider the effect of heat and mass transport on chemical reactions.

The general method for the construction of mathematical models for complex chemical reactions which allow the calculation, with the aid of analogue computers, of the kinetic characteristics of reactions of any order taking into account the non-isothermal conditions of the process, and also the calculation of the parameters of reactor control systems, has been described by Biryukov and Kafarov [99]. They also described the ideas underlying the element-by-element calculation by analogue computers of the parameters of various models of industrial chemical reactors [100-102].

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GAS CHROMATOGRAPHY IN CATALYTIC STUDIES

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I. INTRODUCTION

The development of gas chromatography opens up wide possibilities in the study of catalytic processes. Gas chromatography makes it possible to obtain in a relatively short time information about the composition of the starting materials and products in catalytic processes, facilitates tests on catalysts, and greatly simplifies the experimental technique. A number of examples have been described of the successful use of gas chromatography in the analysis of the products of catalytic processes such as hydrogenation[1-5], dehydrogenation[6-8], isomerisation[9-12], dealkylation[13-15], oxidation of organic and inorganic substances[16-18], polymerisation[19-21], and reactions of organosulphur compounds derived from petroleum[22-24] and of other substances.

In many cases the method in which the catalytic reaction is performed in a flow microreactor attached directly to a chromatographic column proved very fruitful[25-29]. The use of labelled atoms in radiochromatography has been an effective means of studying the mechanism of catalytic processes[28,30,31].

Considerable interest attaches also to catalytic reactions under chromatographic conditions[30-33], whereby it is possible to obtain rapidly new, valuable data on the mechanism and the kinetics of the process and on the properties of the catalyst and their variation with time.

Finally, gas chromatography is a rapid method for the determination of the isotherms and heats of adsorption, the specific surfaces of catalysts, and their surface structure, acidity, and catalytic activity[34-39].

II. QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE PRODUCTS OF CATALYTIC PROCESSES

The study of the majority of catalytic processes is impossible without qualitative and quantitative analysis of the initial materials and the reaction products. In these studies gas chromatography often proves to be the most effective analytical method both in laboratory tests and in the control of industrial processes[40-44].

The methods of analysis of the products of catalytic processes must as a rule meet very stringent requirements, particularly if the reactions are fast and rapid analysis is necessary. For this reason, the shortening of the duration of analysis while maintaining adequate capacity for separation and adequate precision is one of the principal requirements which must be satisfied by a gas-chromatographic method. In many catalytic processes very complex mixtures of substances of different types are obtained, the concentrations of the individual components varying between very wide limits[6,40,41,45]. It is very difficult to separate such mixtures and to analyse them qualitatively and quantitatively.

On the other hand, the determination of trace impurities in the starting materials or the catalytic reaction products is no less complex a problem[46]. The total analysis of the products is frequently interfered with by the presence in the latter of unstable or reactive compounds, substances tending to polymerise, and also water[16,47-49]. It is therefore often necessary to perform extensive preliminary experiments in order to find the most favourable conditions for the chromatography of such mixtures.

Qualitative analysis. Qualitative analysis in gas chromatography is usually concerned in the first place with