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Present State of the Theory of the Chromatographic Microreactor

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Published information on the use of a pulse chromatographic microreactor in catalytic investigations is reviewed systematically. Theoretical analysis of the processes occurring in such a reactor showed the possibility of using transient pulse methods to determine the adsorption and desorption rate constants for starting materials and products during a catalytic process, to study the effect of longitudinal and internal diffusion, to reveal the principal and subsidiary paths of complicated catalytic processes, etc. From an analysis of published data it is concluded that chromatographic methods should be introduced more widely to solve complex kinetic problems in heterogeneous catalysis. A list of 90 references is included.

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I. INTRODUCTION

The invention in 1955 of the microcatalytic reactor, by Kokes et al. [1] just three years after Martin had formulated the principles of gas–liquid chromatography [2], advanced significantly the range of application of chromatography in catalysis. In essence the method is extremely simple: the reactor filled with the test catalyst is inserted into the gas circuit in front of the chromatographic column of an ordinary gas chromatograph. The microreactor is placed in a furnace to ensure a specified temperature in the catalyst bed, and a stream of an inert carrier gas is passed through continuously. A specified quantity of the reactant is periodically introduced as pulses into the microreactor. The reaction products and the unchanged material are carried into the chromatographic column by the stream of carrier gas.

Several modifications of the pulse method have now been described, but they all have the common features of rapidity, the possibility of using very small quantities of reactants and catalysts, and also great sensitivity [3].

Use of the microcatalytic reactor yielded within a short time voluminous and important information on both processes and catalysts for several important systems [4-6]. With highly sensitive detectors and efficient separating columns any side reaction, which might remain unnoticed in the usual method, could be recorded as well as the main reaction. In several cases we can begin to discern the chief features of the step-by-step mechanism of certain complicated reactions. It is already difficult to imagine a modern catalysis laboratory in which wide use would not be made of the microcatalytic reactor, together with the usual catalytic equipment, especially for the selection of new catalysts [7-10].

The present paper surveys the kinetics of catalytic reactions taking place in a microcatalytic reactor with the pulsed introduction of reactants. The kinetics of a process in a microcatalytic reactor may in general differ significantly from the kinetics in the flow-type and circulatory apparatus traditionally used for catalysis. We must distinguish several groups of factors responsible for these differences.

The first group depends on the difference in the state of the catalytic surface. In the microreactor the catalyst is continuously blown out at the reaction temperature by the stream of pure inert carrier gas.

Since a pulse usually introduces a very minute quantity of reactant into the microcatalytic reactor, results obtained for the first few pulses can often be regarded as representing the catalytic properties of a surface not yet subjected to the action of the reacting system. By introducing pulse after pulse or reactant into the microreactor, it is possible to trace a gradual change in catalytic activity during the catalytic process; this opens up the possibility of studying kinetics on catalysts operating under transient conditions. Belousov has paid close attention to this problem in a series of studies [11-13] of the mild oxidation of propene on a large number of oxide catalysts. When tested under steady-state conditions, the catalyst remains for a long time in contact with the reaction mixture, so that its surface is able to undergo significant changes. Many investigations have shown that the catalytic activity of a catalyst measured from the first few pulses in the microreactor sometimes exceeds by several powers of ten the activity determined under steady-state conditions.

The second group of factors responsible for the distinctive features of processes occurring in the microreactor depend on the movement of bands of starting materials and products along the catalyst layer, and also on the changes in the concentration profile and surface coverage resulting from diffusion, adsorption and desorption, etc. We shall examine below the effect of these processes on the kinetics of catalytic reactions in the microreactor.

II. IRREVERSIBLE REACTIONS

1. Reactions of Type A → B with a Linear Adsorption Isotherm for A, Rapid Establishment of Adsorption Equilibrium, and Absence of Diffusion Processes

An account of the theory of processes occurring in the microcatalytic reactor can easily begin with the simplest case, in which adsorption of the reactant A on the catalyst is rapid and is described by the linear Henry equation

$$a_A = \Gamma_A c_A \tag{1}$$

and the effect of diffusion on the blurring of the band can be neglected. Here c_A and a_A are the concentrations of A in gaseous and adsorption media respectively, while Γ_A is the Henry coefficient.

If we write the equation of continuity for flow of substance A across an elementary layer in the microcatalytic reactor, and take into account Eqn. (1) and the appropriate boundary conditions, we obtain a linear partial differential equation[14]. By solving this equation we can determine the concentration $c_A(x, t)$ of the reactant A in any cross-section x of the column at a specified time t:

$$c_A(x, t) = \psi(t - t_R)\exp(-t_R^{corr} k) \tag{2}$$

where $\psi(t)$ is a function describing the shape of the pulse fed to the microreactor, t is the time measured from the introduction of the pulse, t_R and t_R^{corr} are the usual parameters of a chromatographic experiment—the retention time and the "corrected" retention time[15] respectively—and k is the first-order rate constant of the heterogeneous catalytic reaction.

Equation (2) shows that the pulse of reactant A moves along the catalyst layer at a constant speed with a gradually diminishing height but without change in its original width. In this simple case the reaction rate constant can easily be determined by means of an equation analogous to the formula for a flow reactor:

$$k\Gamma = \frac{1}{\tau}\ln\frac{1}{1-\alpha} \tag{3}$$

where $\tau = v_{cat}/u_{vol}$, in which v_{cat} is the volume of catalyst in the microreactor and u_{vol} the space velocity of the carrier gas through the reactor; α is the degree of conversion, usually determined from the ratio of the peak area for A at the outlet from the microreactor to the corresponding area at the inlet.

For a first-order reaction α is independent of the distribution of the initial substance A along the reactor layer, i.e. on the form of the pulse. This enabled Habgood and Basset[16] to deduce Eqn. (3) without setting up differential equations relating the form of the pulse with time and position. This equation has been widely used to analyse experimental results obtained with the microcatalytic reactor[17,18]. Incidentally, experimental verification that α is independent of the form of the initial pulse for a first-order reaction has been reported in several papers[19,20].

Roginskii and Rozental'[21] examined the simultaneous occurrence of heterogeneous and homogeneous reactions in the microcatalytic reactor. Their solution was analogous to (2) with the constant k replaced by an effective constant

$$k_{eff} = \frac{(1-\varkappa)k\Gamma_A + \varkappa k^{hom}}{\varkappa + (1-\varkappa)\Gamma_A} \tag{4}$$

in which k and k^{hom} are the rate constants of heterogeneous and homogeneous reactions respectively, and $\varkappa$ is the free volume of the batch. The observed activation energy of the reaction E_{obs} can be determined from the temperature variation of k_{eff}. If only a heterogeneous reaction takes place in the reactor, we have

$$E_{obs} = E_{true} - Q_{ads} \tag{5}$$

When only a homogeneous reaction occurs, then

$$E_{obs} = E_{true} \tag{6}$$

Ample information on the kinetics of a reaction of type A → B in the microreactor can be obtained[22-25] from the form of the peak for product B recorded immediately beyond the microreactor. The form of this peak was described by solving the set of differential equations for the material balance of A and B with linear adsorption isotherms.

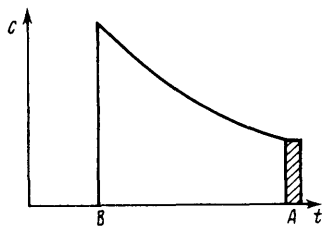


Figure 1. Diagram of chromatogram obtained directly after reactor, for the reaction A → B.

It was supposed[24,25] that a narrow band of the starting material A of width δ had been introduced into the originally empty microcatalytic reactor. The following picture of the movement of the bands of A and B along the catalyst bed emerges from these results. On the right of Fig. 1 is shown hatched the band of reactant A, which, without changing its initial width δ, moves at a speed inversely proportional to Γ_A, while gradually diminishing in height (e.g. Eqn. 2). The right-hand boundary of band B is adjacent to band A and moves at the same speed. The left-hand boundary of band B moves at a speed determined by the coefficient Γ_B. Thus the width of band B is governed by the difference $\Gamma_A - \Gamma_B$ and the form by the rate constant k. The retention time of band B can usefully be determined from the elution time of the centre of gravity of the band t_{cg}^B, for which the relation

$$t_{cg}^B = t_A^R + \frac{\Gamma_A - \Gamma_B}{\Gamma_A k} + \frac{t_A^R}{\alpha}\left[\frac{\Gamma_B}{\Gamma_A} - 1\right] \tag{7}$$

has been obtained[25]. For rapid reactions ($k \to \infty$, $\alpha \to 1$) it follows from (7) that

$$t_{cg}^B = t_A^R \frac{\Gamma_A}{\Gamma_B} \tag{8}$$

With small degrees of conversion

$$\alpha \approx 1 - \exp(-k t_R) \approx k t_R$$

we find that

$$t_{cg}^B \approx {}^1/_2 t_A^R \cdot \left(1 + \frac{\Gamma_B}{\Gamma_A}\right) \tag{9}$$

It has been shown also that the blurring of the band of products B is proportional to the square of the relative difference between the Henry coefficients for A and B, and depends also on k and α:

$$\sigma_B^2 = \left(\frac{\Gamma_A - \Gamma_B}{\Gamma_A}\right)^2 \left[\frac{1}{k^2} - \frac{t_A^R}{\alpha}\left(\frac{1}{\alpha} - 1\right)\right] \quad (10)$$

Formulae (7) and (10) can be used for the experimental determination of k and Γ_B.

Calculations have been made [22,23] of the form of the hydrogen band produced by dehydrogenation when a broad rectangular pulse of cyclohexane is admitted to a microreactor filled with a platinum–alumina catalyst. The microreactor was followed by a column containing activated carbon, which completely absorbed unchanged cyclohexane and the benzene formed, while hydrogen passed through. From the shape of the hydrogen band it was possible to calculate the reaction rate constant k and the activation energy for the dehydrogenation of cyclohexane to benzene.

2. Reaction of Type nA → B with a Linear Adsorption Isotherm for A and Rapid Establishment of Adsorption Equilibrium

The progress of an irreversible reaction of order n with a linear adsorption isotherm for the starting material A and rapid establishment of adsorption equilibrium has been considered in the paper cited above [14]. The equation of material balance together with the linear isotherm yields the solution

$$c_A(l, t) = \frac{\psi(t - t_{cg}^R)}{\sqrt[n-1]{1 + (n-1)\, k t_A^{coff} \Gamma_A^{n-1} \psi^{n-1}(t - t_R^A)}} \quad (11)$$

where $\psi(t)$ is the form of the entering pulse and l the length of the catalyst bed. The self-evident relation

$$1 - \alpha = \frac{\int_{t_A^R}^{T + t_A^R} c_A(l, t)\, dt}{\int_0^T \psi(t)\, dt} \quad (12)$$

exists between α and the size and shape of the pulse of A at the inlet to the microreactor. From Eqns. (11) and (12) expressions have been obtained [14] for calculating the constants k from definite experimental values of α with $n = 0$, 1, 2 for rectangular and triangular pulses.

It is possible to determine n and k by conducting the reaction at small values of α in the microreactor [28]. The rate w of a catalytic reaction in the microreactor can be written

$$w = \frac{\Delta m}{\Delta t \cdot v_{cat}} \quad (13)$$

where Δm is the quantity of material converted and Δt the residence time of the reactant band on the catalyst bed of volume v_{cat}. Although α depends on the form of the pulse when $n \neq 1$ the differences do not exceed 10–15% if pulses having the same mean concentration c_{av} are compared. The reaction velocity in the microreactor can therefore be related to the mean concentration in the pulse, and a correction then made for the shape of the latter:

$$w = \frac{\Delta m}{\Delta t \cdot v_{cat}} = k_{eff} \Gamma^n c_{av}^n \quad (14)$$

in which $k$eff is an effective rate constant based on c_{av}.

It follows from (14) that the order of the reaction is determined from the slope of the linear plot of lg w against lg c_{av}, and $k$eff from the intercept made by this straight line on the vertical axis. To determine the true rate constant k we must introduce a correction for the form of the pulse:

$$k = k_{eff} \frac{\left[\frac{1}{T}\int_0^T \psi(t)\, dt\right]^n}{\frac{1}{T}\left[\int_0^T \psi^n(t)\, dt\right]} \quad (15)$$

This equation was obtained by expanding formula (11) for the elution curve as a Taylor series, and substituting the approximate value of $c_A(l, t)$ in (12). Germain [28] obtained an analogous expression by a somewhat different method.

When $n = 0$ or 1 the correction calculated from the ratio of integrals on the right-hand side of Eqn. (15) is unity: i.e. $k$eff $= k$ for reactions of zero and first order, independently of the form of the pulse. In the case of rectangular pulses this correction can be shown also to be unity for any value of n.

The above method has been used [29] to study the oxidative dehydrogenation of isopentenes to isoprene on a catalyst comprising a mixture of the oxides of iron, chromium, and zinc.

If the order of the reaction is determined from (14) and substituted in (11), the approximate formula

$$(1 - \alpha)^{1-n} = (n - 1)\, c_{av}^{n-1} k \Gamma^n \tau \quad (16)$$

can be obtained instead of the input function of the mean concentration c_{av} in the pulse. This gives another simple procedure for determining the apparent rate constant [27]. The slope of the dependence of $(1 - \alpha)^{1-n}$ on τ is $(n - 1)k\Gamma_A^n c_{av}^{n-1}$. Determining c_{av} from the form of the pulse at the inlet to the microreactor, we can calculate the approximate value of $k\Gamma_A^n$ by dividing the slope by $(n - 1)c_{av}^{n-1}$.

3. Effect of Diffusion on an nth-Order Reaction of Type nA → B

An examination has been made [30] of the kinetics of nth-order reactions with longitudinal diffusion and rapid establishment of adsorption equilibrium. Since the diffusion equations are non-linear in this case, a mathematical solution cannot be obtained. We therefore assumed that the reaction had no significant effect on the blurring of the band of the initial substance. This can be expressed mathematically by writing

$$c_A(x, t) = c_A^0(x, t)\, N(t)$$

where $c^0(x, t)$ is the solution of the corresponding problem for gas-adsorption chromatography in the absence of reaction, and $N(t)$ is a function of time. If the relation

$$\frac{dc_A}{dt} = k\Gamma^n c_A^n(x, t),$$

is satisfied at every point in the bed, integration with respect to x and substitution of the preceding expression for $c_A(x, t)$ yields for $N(t)$ an ordinary differential equation, whose solution presents no difficulty. This is fully analogous to the approach used by Frank-Kamenetskii [31].

To summarise the principal qualitative results[30], diffusion has hardly any effect on the degree of conversion in first-order reactions ($n = 1$). Longitudinal diffusion slows down the reaction more strongly the higher the order of the reaction above unity. With second-order reactions the rate decreases in proportion to the square root of the time, owing to the diminution in the concentration in the reaction zone caused by blurring of the band. This effect becomes greater with increase in the length of the reactor bed and decrease in the rate of flow.

4. Reaction of Type A → B with Slow Establishment of Adsorption Equilibrium

In order to discuss the progress of a first-order reaction in a microcatalytic reactor taking into account the kinetics of adsorption[21] the usual material balance equation was solved together with the differential equation of sorption kinetics

$$\frac{\partial a_A}{\partial t} = k_A^a c_A - (k + k_A^d) a_A \qquad (17)$$

in which k_A^a and k_A^d are the rate constants of the adsorption and the desorption of substance A. An expression was obtained[21] for the form of the elution curve of A which included Bessel functions.

In the Reviewers' opinion it is more convenient, in the experimental determination of the rate constants k, k_A^a, and k_A^d, to use the expressions for the main parameters of the peaks of starting materials and products that can be obtained by the statistical method of moments[32]:

$$1 - \alpha = \exp\left\{-\frac{x}{u}\left[\frac{(1-\varkappa)\,k_A^a k}{(k + k_A^d)}\right]\right\} \qquad (18)$$

$$t_A^R = \frac{x}{u}\left[\varkappa + \frac{(1-\varkappa)\,k_A^a k_A^d}{(k + k_A^d)^2}\right] \qquad (19)$$

$$\sigma_A^2 = \frac{2x}{u}\frac{(1-\varkappa)\,k_A^a k_A^d}{(k + k_A^d)^3} \qquad (20)$$

where u is the linear rate of flow and σ_A^2 is the dispersion of the concentration distribution at the exit from the reactor.

With regard to the physical significance of the results, if the reaction occurs in the kinetic range ($k \ll k_A^d$), Eqn. (18) passes into Basset's well known equation (3). Thus Eqn. (3) applies (as is usually supposed) not only when adsorption equilibrium is established instantaneously but also in the more general kinetic case with $k \ll k_A^d$. With this last condition it follows from Eqns. (19) and (20) that even the occurrence of a heterogeneous reaction has no effect on the retention time or the blurring of the reactant A band. If k and k_A^d are comparable, the occurrence of a reaction accelerates movement of the A band and diminishes blurring. When desorption is the limiting stage ($k \gg k_A^d$), the corrected retention time $t_A^{R\,corr}$ is inversely proportional to k^2, while σ_A^2 is inversely proportional to k^3.

If it is assumed that the initial substance A and the product B are sorbed independently, and that the adsorption of both substances conforms to a linear kinetic equation, it appears possible to study the kinetics of the catalytic reaction from the form of the B band. In this case[25] the set of equations for A must be supplemented by the material balance equation and the linear kinetic equation describing the movement of the B band. This set of equations has recently been solved by an operational method[25], to yield expressions for the retention time t_B and the dispersion of the band σ_B^2 of product B analogous to those obtained for A (Eqns. 18–20). Thus the retention time is

$$t_B = t_A + \frac{x(1-\varkappa)}{\alpha u}[\Gamma_B - \Gamma_A^{eff}] - \frac{k_B^a(k + k_A^d) - k_A^a(k + k_B^d)}{k \cdot k_B^d \cdot k_A^a} \qquad (21)$$

where $\Gamma_A = k_A^a k_A^d/(k + k_A^d)^2$ is the effective Henry coefficient for the starting material. It follows from (21) that the elution time of the reaction product should differ from its retention time in gas-adsorption chromatography, as has been confirmed experimentally[25]. In a study of the cracking of cumene on an aluminosilicate catalyst, a mixture of benzene and cumene was introduced into the reactor. The chromatogram obtained immediately following the reactor shows (Fig. 2) separate peaks for benzene added to the reactor and for benzene produced in the reaction.

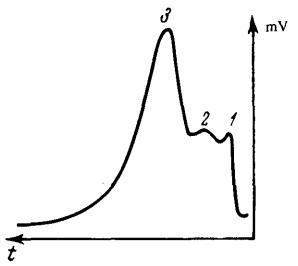


Figure 2. Chromatogram obtained after the microcatalytic reactor for the cracking of cumene on an aluminosilicate catalyst. A mixture of benzene and cumene was introduced into the reactor: 1) benzene added to the reactor; 2) benzene produced by the cracking of cumene; 3) cumene.

When $\Gamma_B = \Gamma_A^{eff}$, i.e. when the adsorption coefficients of starting material and product coincide, it follows from (21) that

$$t_B = t_A + \frac{1}{k_B^d} + \frac{1}{k + k_A^d} \qquad (22)$$

Thus even when $\Gamma_B = \Gamma_A^{eff}$ the peak of the product lags behind the peak of the initial substance a constant distance depending on the rate constant of the heterogeneous reaction and the desorption rate constants of starting material and reaction product.

An experimental method was also proposed[25] for studying the kinetics of adsorption during a catalytic reaction, involving the use of Eqns. (18)–(21) and corresponding expressions for complicated cases. The main difficulty to be overcome was that in this case the characteristics of the peaks due to individual substances at the outlet from the reactor were required for the calculation. Under normal conditions the separation of the components on the catalyst bed is seldom sufficient for direct measurements to be made. It was therefore suggested that the additivity

relations applicable to the reactor–column system[3] should be used:

$$t_c^R = t_p^R + t_\kappa^R$$
$$\sigma_s^2 = \sigma_r^2 + \sigma_{col}^2 \quad (23)$$

where t_S^R and σ_S^2 are the retention time and the dispersion of the peak of a substance which has passed successively through the reactor and the column, t_r^R, σ_r^2 are the retention time and the dispersion of the peak of the substance after passing through the reactor, and t_{col}^R and σ_{col}^2 are the corresponding parameters for the peak after the substance has passed through the column.

The parameters t_S^R and σ_S^2 were determined from chromatograms at the outlet from the separation system, and t_{col}^R and σ_{col}^2 in a separate series of experiments in which a certain quantity of starting materials or products was introduced directly into the separating column. After this t_r^R and σ_r^2 were determined by means of Eqns. (23). This method was used to calculate the adsorption and desorption rate constants for cumene during cracking on an aluminosilicate catalyst.

5. Reactions of Type A → B in the Internal-diffusion Range

The method of moments was used by Rozental'[33] to analyse a complex case of movement of the band of substance A along the bed of the microcatalytic reactor, accompanied by a first-order reaction occurring in the inner-diffusion range. The analysis took into account also the kinetics of the adsorption of A on the internal surface of the catalyst. Effects of longitudinal diffusion were neglected. A set of three equations—(1) the kinetics of adsorption and the first-order reaction, (2) diffusion into the pores, and (3) material balance in the space between catalysts particles—was solved for this model. Application of the Laplace transformation to these equations yielded expressions for α, t_A^R, and σ_A^2 in terms of certain functions $f_0(z)$, $f_1(z)$, and $f_2(z)$ of the dimensionless variable $z = k\Gamma R^2/D_i$, in which R is the particle size of the catalyst and D_i the coefficient of internal diffusion.

The dimensionless parameter z defines the combined effects of adsorption, internal diffusion, and reaction on the form of the elution curve, while $f_0(z)$, $f_1(z)$, and $f_2(z)$ represent the effects of variation in α, t_A^R, and σ_A^2 as a result of diffusion in the pores during the reaction. Each of these functions decreases simultaneously with z and becomes unity when $z = 0$. This case corresponds to the absence of reaction or to rapid internal diffusion.

The function $f_0(z)$ is termed the fractional accessible surface[33]. It increases with decrease in Γ, k, and R; and decreases with decrease in D_i. Increase in $f_0(z)$ is accompanied by increase in α.

The quantity $\Gamma f_1(z)$ constitutes an effective adsorption coefficient. Diffusion combined with reaction diminishes the elution time of the peak of A. The contribution to dispersion due to the slowness of adsorption was also examined[33]. The occurrence of reaction was found to diminish the blurring due to diffusion into the pores.

6. Reactions of Type A → B allowing for Longitudinal Diffusion and Sorption Kinetics

The combined effect of adsorption kinetics and longitudinal diffusion on an irreversible first-order reaction has been examined by Kočirik[34]. The equations for the material balance and the adsorption kinetics of A are written

$$\varkappa \frac{\partial c_A}{\partial t} + (1-\varkappa)\frac{\partial a_A}{\partial t} + u\frac{\partial c_A}{\partial x} + k(1-\varkappa)a_A = D\frac{\partial^2 c}{\partial x^2}$$
$$\frac{\partial a_A}{\partial t} = k_A^a c_A - (k_A^d + k)a_A$$

where D is the coefficient of longitudinal diffusion.

The expressions for α and t_A^R obtained by the method of moments are

$$\alpha = 1 - \exp\left[\frac{u}{2D} - \frac{u}{2D}\sqrt{1 + \frac{4D(1-\varkappa)k \cdot k_A^d}{u^2(k+k_A^d)}}\right] \quad (a)$$

$$t_A^R = \frac{x}{u}\left[\varkappa + \frac{(1-\varkappa)k_A^a \cdot k_A^d}{(k+k_A^d)^2}\right]\frac{1}{r} \quad (b) \quad (24)$$

where r denotes the square-root term in (24a). If the longitudinal diffusion coefficient D is small, Eqn. (24a) passes into (18). In general, however, diffusion combined with reaction accelerates the movement of A. Since r contains u^2 in the denominator, the effect of diffusion will be appreciable at low rates of flow.

An expression was also obtained[34] for the blurring of the band of A. In order to determine r and D experiments must be made at low rates of flow u; then k_A^a and k_A^d can be calculated from experimental results at high rates of flow.

7. Plate Theory of Heterogeneous Catalytic Processes in a Microreactor

The above discussion shows that considerable mathematical difficulties are involved in allowing for the simultaneous effects of adsorption kinetics and internal and external diffusion on retention times and dispersions. Several investigators have therefore tried to approach a solution to this problem on the basis of the "plate theory" employed in chromatography, which makes it possible to establish the effects of experimental parameters on the blurring of bands, although it will not reveal the mechanism of all the processes occurring in a column.

Kallen and Heilbronner[35] were the first to use the plate theory to analyse a process occurring in a microcatalytic reactor. On the assumption that the reaction A → B took place on every plate, differential equations were written for the material balance with respect to A and B. After solution by means of Laplace transformations, these yielded the following expression for the retention volume of A

$$v_{A\ reactn}^{R\ corr} = \frac{v_A^{R\ corr}}{1 + \frac{kv_A^{equiv}}{u_{vol.}}} \quad (25)$$

Here $v^{R\,corr}$ is the corrected retention volume of A in the absence of reaction, and v_A^{equiv} the volume of developer necessary for the complete transfer of A from the nth to the $(n+1)$th plate.

Formula (25) is a qualitative indication of the same relations as obtained in preceding subsections, which allowed for adsorption kinetics and diffusion in analysing the process occurring in the microcatalytic reactor. In fact it follows from (25) that the reactant A moves more rapidly than in the absence of reaction, which is consistent with conclusions reached earlier for non-equilibrium

adsorption. The change in retention volume due to the reaction increases with increase in k. The retention volume decreases also with increase in v_A^{equiv}, i.e. with increase in the time required for the establishment of adsorption equilibrium.

The effect of reaction on the width b_A of the reactant A can also be assessed. On the basis of chromatographic theory[35] the width is determined by means of the relation

$$b_A = \frac{4\, v_A^R}{\sqrt{N}} \tag{26}$$

where N is the number of plates. According to (25) we have $v_A^{R\ reactn} < v_A^R$; therefore the width of the peak of reactant A is less than the width in the absence of reaction.

The equation

$$k = \frac{N\,(1 - \sqrt[N]{1-\alpha})}{v_A^{R\ reactn}}\, u_{vol} \tag{27}$$

has been obtained to calculate k from data at different rates of flow of the carrier gas. Thus by determining α, $v_A^{R\ reactn}$, and N for different rates of flow it is possible to calculate the reaction rate constant.

Nakagaki and Nishino[36] calculated k for the catalytic isomerisation of cyclopropane into propene on a 13X molecular sieve, some of whose cations had been replaced by Ni^{2+}, using the catalytic chromatogram given by Basset and Habgood[16]. The equations for the profile of bands A and B obtained by means of the plate theory enabled several relations for the main characteristics of the peaks to be calculated[36] from the extent of reaction; these were qualitatively consistent with results obtained previously including kinetics and diffusion when analysing processes occurring in the microcatalytic reactor.

III. REVERSIBLE REACTIONS OF TYPE A ⇌ B

Two different approaches have been made to a theoretical analysis of reversible first-order reactions occurring in a microcatalytic reactor: in some papers the equations of material balance and kinetics have been solved; others have given a statistical treatment of the phenomenon, based on a probability study of the behaviour of molecules.

The reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

has been examined[37] with instantaneous establishment of adsorption equilibrium and absence of diffusion complications. The statistical theory developed enables the concentration profile of A and B inside the microcatalytic reactor to be calculated for various series of parameters. The analyses show that, if a mixture of A and B is introduced into the microreactor, a broad band is formed initially, with peaks at the edges corresponding to A and B individually. After some time the band deforms into a single narrower peak containing both A and B in the equilibrium concentrations.

Klinkenberg[38] considered the occurrence of reversible reactions in a microreactor from a rather different point of view. In the case of linear adsorption, with instantaneous establishment of adsorption equilibrium and absence of diffusion complications, the material balance equation is written

$$u\frac{\partial c_A}{\partial x} + \varkappa\frac{\partial c_A}{\partial t} + (1-\varkappa)\frac{\partial a_A}{\partial t} = k_2 a_B - k_1 a_A = \left[u\frac{\partial c_B}{\partial x} + \varkappa\frac{\partial c_B}{\partial t} + (1-\varkappa)\frac{\partial a_B}{\partial t}\right] \tag{28}$$

Comparison of the result obtained by Klinkenberg on solving (28) with the result from Giddings' statistical method shows the same qualitative pattern. When a mixture of molecules of A and B is introduced into the microreactor, the peaks due to these components should disappear as equilibrium is approached, while an intermediate band containing molecules of A and B in equilibrium concentrations will steadily contract, approaching the width of the equilibrium band. The retention time of the equilibrium mixture is written

$$t_{AB}^{R\ eq} = \frac{x}{u}\,\frac{\frac{k_1}{\Gamma_B}[\varkappa + (1-\varkappa)\Gamma_B] + \frac{k_2}{\Gamma_A}[\varkappa + (1-\varkappa)\Gamma_A]}{\frac{k_1}{\Gamma_B} + \frac{k_2}{\Gamma_A}} \tag{29}$$

If a mixture of equilibrium composition is introduced into the microreactor, it will move at a mean speed, and emerge as a single peak after time $t_{AB}^{R\ eq}$. Thus, when for any reason it is important to avoid the occurrence of a reversible reaction in an analytical chromatographic column, a kind of "chromatographic azeotropy" will be observed, such that A and B will not be separated under the given conditions despite significant differences in ΓA and ΓB.

IV. THEORY OF REACTIONS UNDER CHROMATOGRAPHIC CONDITIONS

The separation of products and starting materials on the bed of the microreactor has a considerable effect on the course of the catalytic process. We shall show below, for example, that with reversible reactions the spatial separation of products or reactants has a significant effect on the degree of conversion by completely or partly suppressing the reverse reactions. In the case of consecutive reactions the separation of substances on the catalyst bed sometimes changes fundamentally the selectivity of the process.

The action of poisons will also be different under conditions of separation. Because of the difference in adsorption coefficients between poison and reactant, the poison band may not enter the reaction zone at all, and therefore not poison the catalytic process. Similar phenomena will sometimes be observed in the self-poisoning of the reaction by the products.

Finally we note that, with non-first-order reactions, the kinetics of the catalytic process is influenced also by the form of the concentration profile in the reaction zone, governed, as noted above, by the kinetics of adsorption and desorption, external and internal diffusion, etc.

The above features led us to combine in the same section cases in which the yield or the selectivity of the reaction is influenced by various chromatographic effects. Such reaction conditions in the microcatalytic reaction have been termed[39] "chromatographic". Theory shows[37] that the character of a chromatographic process is determined by the method used to move the chromatographic band along the layer of stationary phase. A chromatographic régime can therefore be established in various specific forms. We shall consider below mainly the elution

type of chromatographic process, which has recently been subjected to the most thorough theoretical analysis. However, this by no means exhausts the possibilities of the method.

1. Reaction of Type A ⇌ B + C

The equations describing processes occurring in the microcatalytic reactor with such reactions are non-linear. For the sake of simplicity, therefore, we shall consider only the case of a linear adsorption isotherm and instantaneous establishment of adsorption equilibrium. Let us examine first some general considerations[39].

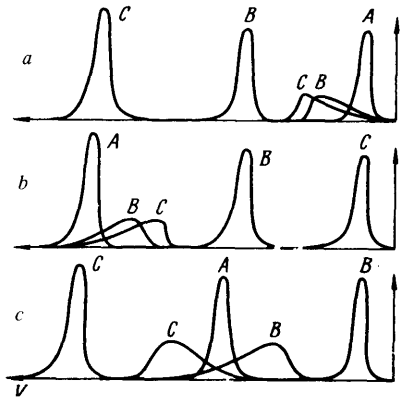


Figure 3. Diagram illustrating the establishment of a chromatographic régime.

Fig. 3 illustrates three possible relative arrangements of the A, B, and C bands on the catalyst bed, corresponding to the three relations among the adsorption coefficients —(*a*) $\Gamma_C > \Gamma_B > \Gamma_A$, (*b*) $\Gamma_A > \Gamma_B > \Gamma_C$, and (*c*) $\Gamma_C > \Gamma_A > \Gamma_B$. In case (*c*) (Fig. 3) the introduction of a narrow band of A should lead almost to cessation of reaction from right to left. In cases (*a*) and (*b*) the reverse reaction will be more strongly inhibited the larger the absolute difference $\Gamma_B - \Gamma_C$. This possibility of carrying out reversible reactions in one direction under chromatographic conditions was pointed out in Ref. 39, and has since been confirmed experimentally[40,41].

Magee[42] considered a reaction of type A ⇌ B + C under conditions such that its progress was limited solely by the equilibrium constant $K = c_B c_C / c_A$. He wrote down the equation of material balance, and solved it for the appropriate equilibrium condition by means of an analogue computer. He showed that with $K = 10^{-7}$ the reaction may be complete in a column 1 m long after only 17 s. It must be stressed that such large chromatographic effects, even with such small equilibrium constants, are due to the ideal character of the model, which disregards kinetic and diffusion effects. The displacement of equilibrium actually observed will always be smaller than the calculated shift.

To allow for the kinetics of a heterogeneous process with the present type of reaction under chromatographic conditions in a pulse microcatalytic reactor[27] the calculations are simplified by supposing that $\Gamma_A = \Gamma_C \neq \Gamma_B$.

Fig. 4 shows the dependence of α on the length of the layer calculated on an electronic computer. It is evident that α is significantly greater under chromatographic conditions than under dynamic conditions, but rather lower than for an irreversible reaction.

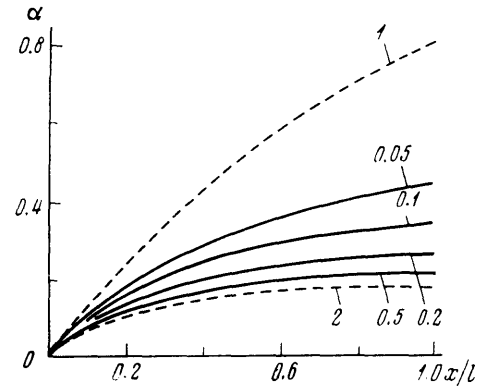


Figure 4. Dependence of degree of conversion α on dimensionless length x/l of catalyst bed for reaction of type A ⇌ B + C occurring under chromatographic conditions for different pulse widths τ_0 (numerals on full curves): 1) irreversible reaction; 2) flow-type reactor.

Hitherto we have been considering a single introduction of A into the microcatalytic reactor. However, if an attempt is made in the future to exploit in some measure the above chromatographic effects to develop a new technical process, the question should, of course, be raised of the possibility of introducing many such pulses into the reactor and of the interaction on the catalyst bed between bands from different pulses. Roginskii and Rozental'[43] tried to assess these effects by using an electronic computer to obtain calculated curves showing the dependence of α on length of bed for different durations of pulse and different intervals between their introduction. In all cases in such a cyclic process α reaches a maximum value in a reactor having an optimum bed length l_{opt}. The yield of reaction products could be increased by the chromatographic effects with a specified supply of starting material to the dynamic reactor and to the microcatalytic reactor.

When calculated values are compared with experimental results it must be borne in mind, however, that the kinetics of adsorption and diffusion were neglected in the above theoretical analysis of reactions of type A ⇌ B + C. In several cases these effects may be significant.

The reality of the chromatographic effects has been confirmed in several investigations. In a typical chromatogram (Fig. 5) obtained directly after the microreactor for the dehydrogenation of cyclohexane $C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$ on a platinum–alumina catalyst[40,44] the peaks due to cyclohexane and to benzene are clearly separated. Since an argon ionisation detector[3], was used, which was very insensitive to molecular hydrogen, the latter was not detected on the chromatogram. Comparison of the curves for the dehydrogenation of cyclohexane under

chromatographic conditions with the equilibrium curve and with the curve obtained in a dynamic reactor showed that chromatographic conditions raised the yield of benzene significantly above the equilibrium value. Matsen et al.[41] have since shown that chromatography can be applied to this system. The presence of chromatographic effects has apparently been recorded also in several other experimental investigations[45,46], in which study of the kinetics of the processes was not a matter of special concern.

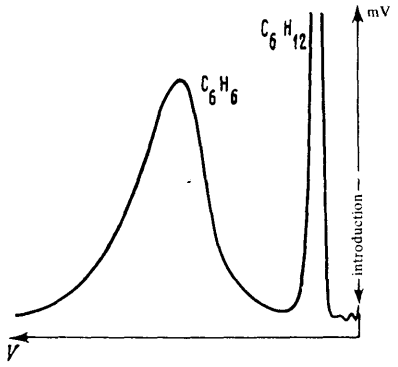


Figure 5. Chromatogram for the dehydrogenation of cyclohexane to benzene on a platinum–alumina catalyst.

2. Reaction of Type A ⇌ 2B

It has recently been shown[47] that reactions of the present type may also be influenced by chromatographic effects, although this cannot now be attributed to the spatial separation of molecules of the products on the bed of the microcatalytic reactor. Numerical calculations have again confirmed an increase in yield in the microreactor in comparison with the dynamic reactor, the difference gradually diminishing with increase in pulse width.

The increase in yield in this class of heterogeneous reactions is due to blurring of the product band resulting from the difference in adsorption coefficients between starting material A and reaction product B. This is entirely analogous to the above blurring of the product band for a first-order reaction. Nevertheless, the nature of the change in the yield occurring under non-stationary conditions in the present case is concealed in the differences between the adsorption coefficients Γ_A and Γ_B. When $\Gamma_A = \Gamma_B$, the effect should disappear.

Under the influence of diffusion the yield of the product may be higher than under stationary conditions even when $\Gamma_A = \Gamma_B$.[30] Since diffusion does not affect the rate of a first-order reaction, but diminishes the rate of reactions of higher order, the rate of the forward reaction will remain unchanged in the present case, whereas that of the reverse reaction ($n = 2$) will decrease. The yield of products B will therefore be higher than at equilibrium.

3. Consecutive Reactions

The main conclusion of the first kinetic analysis of a series of models of consecutive reactions[47] was that chromatographic effects could change significantly the selectivity of the catalytic process in comparison with a dynamic régime. For example, in both the reaction types

$$A \rightarrow B \rightarrow R \qquad R \rightarrow B \rightarrow S \quad (a)$$
$$A \rightarrow R \qquad 2R \rightarrow S \quad (b)$$

the yield y_R of the intermediate product R with a microcatalytic reactor might exceed tenfold the yield in a dynamic reactor. The yield y_R increases with decrease in the width of the entering pulse, since decrease in pulse width intensifies chromatographic effects.

These conclusions[47] were qualitatively confirmed by experimental investigations[48] on the cracking of cumene on an aluminosilicate catalyst in the microreactor. With a sufficiently narrow input peak of cumene yields of benzene exceeded the equilibrium values. The yield increased also when the microcatalytic bed was lengthened. By extrapolating the dependence of α on pulse width to zero, the reverse reaction (alkylation) can be neglected, and the rate constant can be calculated for the forward cracking reaction.

Cracking was accompanied by the disproportionation of cumene with the formation of di-isopropylbenzene[48]. The latter could occur in two possible ways:

$$\text{Cumene} + \text{Propene} = \text{Di-isopropylbenzene} \quad (c)$$
$$2\,\text{Cumene} = \text{Di-isopropylbenzene} + \text{Benzene} \quad (d)$$

In the case of reaction (c) a narrower pulse should give a lower yield of di-isopropylbenzene, since cumene and propene would then be more effectively separated. Since increasing the width of the sample has no effect on the yield of di-isopropylbenzene, it was concluded that catalytic disproportionation takes place in conformity with equation (d).

4. Reactions of Type A ⇌ B + C under a Chromatographic Régime

We have been considering the possible chromatographic effects under isothermal conditions of pulse developmental gas-adsorption chromatography. However, chromatographic separation can be accomplished in several ways[3], e.g. thermal displacement with a constant temperature field[49], chromathermographic[15], with a programmed rise in temperature[3], etc.

Let us consider, for example, the progress of the reaction A ⇌ B + C under the conditions of stationary chromathermography[50] suggested as long ago as 1950 to 1951 by Zhukhovitskii and Turkel'taub[51]. The essence of the method is that a band of material is moved along the bed of the stationary phase not only by a stream of carrier gas (as in the developmental form) but also by the simultaneous action of a moving temperature profile. This is usually accomplished by moving along the layer, in the same direction as the carrier gas, a furnace with a negative temperature gradient (i.e. a furnace in which the temperature is gradually raised will be advanced towards the bed at a speed w_n). The substance A introduced

originally into the microcatalytic reactor will be displaced along the charge, at a rate w_A inversely proportional to Γ_A, at the initial (low) temperature of the microreactor. No reaction will yet occur. During this initial period $w_n > w_A$, so that the band of A will gradually move into a region of higher and higher temperatures, which will accelerate its motion owing to the fall in Γ_A with rise in temperature.

At a certain "characteristic" temperature T_{char} the band of A will move along the layer at the same speed as the furnace. Zhukhovitskii and Turkel'taub showed that, under the conditions of stationary chromathermography, this temperature depends on the heat of adsorption Q_A and the linear rate of flow u of the carrier gas:

$$T_{char} = \frac{Q_A}{R \ln \frac{w_n}{u}} \quad (30)$$

At a given ratio w_n/u the characteristic temperature may be relatively low, and the reaction A ⇌ B + C will not take place. At a certain ratio w_n/u the characteristic temperature may be higher than the temperature T_{str} at which reaction begins. Migration of the band of A will then be accompanied by the formation of B and C, which will converge into zones corresponding to their characteristic temperatures $T_{char,B}$ and $T_{char,C}$. These features make chromathermography extremely promising for the attainment of considerable chromatographic effects. It must be emphasised that the reverse reaction C + B → A can be completely suppressed not only by the spatial separation of B and C on the bed in the microcatalytic reactor, as in the case of the isothermal pulse method, but also by the localisation of at least one of the products B or C (or their mixture) in a low-temperature zone. Thus even a reaction of type A ⇌ B can be conducted in one direction in a chromathermographic microcatalytic reactor.

Use of a chromathermographic microcatalytic reactor is sometimes advisable also because it always involves compression of the bands. Because a negative temperature gradient is present the front of the band, being situated in a cold region, moves more slowly than the rear portion, located in a hotter part of the bed. Since compression of the band entails an increase in concentration in the reaction zone, reactions above the first order must be expected to occur at higher rates than under isothermal conditions. In particular, reactions in which the products have smaller adsorption coefficients than the starting material, e.g. most cracking reactions, can be advantageously accomplished under such a régime.

A "thermal displacement" method can also be used in the absence of a stream of inert carrier gas[49]. Theoretical analysis shows[50] that movement of the furnace along the reactor causes the individual bands of starting materials and products to be situated along the catalyst bed in order of decreasing adsorption coefficients: i.e. the most sorbable substance will be "pressed" closest to the edge of the furnace, this will be followed by a less sorbable substance, and so on. In the case of the reaction A ⇌ B + C with $\Gamma_A > \Gamma_B > \Gamma_C$, for example, substance A will be converted, in the reaction zone adjacent to the furnace, into B and C, which will be removed continuously into the cold zone as adjacent bands of the pure substances. In this way a reversible reaction can be conducted in one direction.

The above considerations show that we are only at the very beginning of the study and the use of chromatographic effects in catalysis. There are grounds for supposing that further work on these lines will open up new prospects.

V. REACTIONS IN MICROREACTOR WITH A LANGMUIR ADSORPTION ISOTHERM

Above we have been considering reactions in the linear Henry range. The Japanese workers Hattori and Murakami[52] have discussed the kinetics of certain model reactions occurring in a microcatalytic reactor with Langmuir adsorption isotherms.

The equation of material balance for the ith component is written

$$\frac{\partial c_i}{\partial t} + q_{max.} \frac{\partial \theta_i}{\partial t} + u \frac{\partial c_i}{\partial t} + w_i = 0 \quad (31)$$

where q_{max} is the quantity of substance adsorbed when the surface is completely covered, θ_i the fraction of the surface occupied by the ith component, and w_i the rate of formation of this component. When equilibrium is established rapidly, the expression for θ_i has the usual form

$$\theta_i = \frac{\Gamma_i c_i}{1 + \sum_{i=1}^{n} \Gamma_i c_i} \quad (32)$$

where Γ_i is the adsorption coefficient of the ith substance. If adsorption equilibrium is reached slowly, equations of type (31) must be solved together with the kinetic equation

$$q_{max} \frac{\partial \theta_i}{\partial t} = w_{ai} + w_i \quad (33)$$

in which

$$w_{ai} = k_i^a \left\{ \left(1 - \sum_{i=1}^{n} \theta_i \right) c_i - \frac{\theta_i}{\Gamma_i} \right\} \quad (34)$$

and initial and boundary conditions are identical with those considered above for a linear isotherm.

The set of equations obtained after the introduction of dimensionless variables was solved by numerical methods for certain specific schemes.

1. Reaction A → R with Rapid Establishment of Adsorption Equilibrium

The dependence of the degree of conversion α on the length of bed was calculated in this case for different values of the parameter $\tau_0 = T/t_R$. Since T is the time of introduction of the pulse, and t_R the retention time of the initial substance, τ_0 is the dimensionless sample width.

It was found that α decreases with increase in τ_0, and reaches a minimum value as $\tau_0 \to \infty$, which corresponds to a flow-type reaction vessel. This result is easily explained by inhibition effects, which, of course, decrease with fall in concentration in the reaction zone. Blurring caused by the non-linearity of the adsorption isotherm is more marked and the degree of conversion is greater the smaller is τ_0. The difference between pulse and flow methods is due mainly to the decrease in concentration in the reaction zone.

2. Reaction A ⇌ R with Rapid Establishment of Adsorption Equilibrium

In this case, too, the degree of conversion is greater for the microcatalytic than for the dynamic reactor, owing to the diminished concentration resulting from blurring of the band. However, α cannot exceed the equilibrium degree of conversion, since blurring accelerates forward and reverse reactions to the same extent.

3. Reaction A ⇌ R + S with Rapid Establishment of Adsorption Equilibrium

For simplicity the case was considered [52] in which $\Gamma_A = \Gamma_S$ and $\Gamma_R = 0$. The degree of conversion in the microcatalytic reactor was shown to be lower than for the irreversible reaction A → R + S but considerably higher than for the reversible reaction A ⇌ R + S in a flow-type reaction vessel. The increase in α is due not only to a decrease in concentration in the pulse but also to chromatographic separation. Therefore the degree of conversion in the microcatalytic reactor increases with decrease in the width of the input pulse.

4. Reaction A → R with Slow Establishment of Adsorption Equilibrium

Differences between processes occurring in the microcatalytic reactor and the process in a dynamic reactor are still more clearly developed in this case, owing to the diminution in concentrations resulting from blurring of the peak and also from the difference in the initial surface coverage. In the microreactor the catalyst surface is unoccupied before the reactant is introduced, so that the rate of adsorption at the front of the band is high, as the denominator in the Langmuir equation is close to unity.

Since coverage in the first cross-section of the catalyst bed increases exponentially with pulse length, conditions can be selected [52] under which the difference in surface coverage between the pulse method and stationary conditions becomes insignificant. For "thin" pulses, however, the differences are very substantial.

Sadovnikov and Kislyuk note [53] that different conditions obtain in the pulse method and in the steady state when the catalytic reaction takes place at low surface coverage $\theta \ll 1$. Under stationary conditions this requires that $k^a < k^d$, but under pulse conditions small values of θ arise from the usual introduction of such a small quantity of starting material into the reactor that only a small part of the catalyst surface can be covered even on complete adsorption. Therefore the first order may be observed in the pulse method, but a fractional or even zero order under flow conditions.

Coverage of the portion of the catalyst bed on which the pulse is located depends also on k^a and k^d. It can be imagined that, when these constants are large (but equilibrium may still not be reached), the whole pulse is grouped on a very tiny part of the layer, where coverage is large. However, the situation described in Ref. 53 is also entirely possible. Unfortunately, to allow for all these factors quantitatively is quite a complicated task, since no analytical solution (even approximate) of the problem has been obtained, and the numerical calculations have been insufficiently detailed. A characteristic feature of this case would probably be variation in the order of the reaction with the volume of the sample at a constant initial concentration.

VI. KINETICS OF REACTIONS IN MICROREACTOR ON NON-UNIFORM SURFACES

Roginskii and Rozental' [54] analysed processes occurring on non-uniform surfaces (with respect to adsorption and catalytic properties) inside a microreactor. The equation

$$\frac{\partial\theta_A}{\partial t} = k_A^a c_A(1-\theta_A) - (k + k_A^d)\theta_A \qquad (35)$$

where θ is the relative coverage of active centres, applies to a group of sites having the same adsorption and catalytic properties. Applying the theory of catalytic processes on non-uniform surfaces [55], these workers obtained formulae for the quantity of substance adsorbed and the rate of the heterogeneous reaction. These enabled in principle equations for the form of elution curve of reactant A to be deduced from a known distribution function of sites with respect to adsorption and desorption rate constants $\rho(k_A^a, k_A^d)$. Analogous relations can be found also for the product B. Since a general solution of these equations presents considerable mathematical difficulty, certain particular cases were considered, for which quite simple expressions were obtained.

At low partial pressures (when $\theta_A \ll 1$), for example, the effect of non-uniformity for any distribution function $\rho(k_A^a, k_A^d)$ is merely to introduce an effective reaction rate constant calculated by means of the equation

$$k_{eff} = N_0 \int\int \frac{kk_A^d}{k_A^d - k} \rho(k_A^a, k_A^d)\, dk_A^a dk_A^d \qquad (36)$$

where N_0 is a constant depending on the number of active centres per unit surface, the specific surface, the density, and the porosity of the catalyst. An equation was obtained [54] enabling k_{eff} to be calculated from the measured quantity of unchanged substance $G(l)$, provided that the diffusion coefficient D was determined by an independent method. With low values of D the usual expression is obtained for a first-order reaction with a rate constant k_{eff} allowing for surface non-uniformity:

$$G(l) \quad G_0 \exp - \left(\frac{k_{eff} l}{u}\right) \qquad (37)$$

Several other limiting cases were examined [54]. When adsorption equilibrium is established on every adsorption site, for example, the equations obtained have the same form as those for uniform surfaces. All the differences are covered by replacing the Henry coefficient and the rate constant of the heterogeneous reaction by integrated mean values for the non-uniform surface. Thus, with a known distribution function and a specified functional variation $k = k(\Gamma)$, the relations obtained for a uniform surface are easily generalised to apply to a non-uniform surface. The above cases by no means completely describe the processes occurring on non-uniform surfaces in a microcatalytic reactor. Future theoretical developments will probably enable the character of the surface non-uniformity with respect to adsorption and catalytic properties to be determined from the shape of the peaks of starting material or product measured under various experimental conditions.

VII. USE OF MICROREACTOR FOR DETERMINATION OF RATE CONSTANTS OF INDIVIDUAL PATHS IN COMPLICATED REACTIONS

It is clear from the above discussion of the kinetic features of the pulse method for studying catalytic reactions that quantitative analysis is at present possible only for relatively simple reactions. Detailed examination of the kinetics of complicated systems is as yet an unsolved problem. Nevertheless, even in this case, the use of a microcatalytic reactor may yield valuable information on the individual paths of a complex process. We shall confine the present Section to an analysis of the simplest cases of first-order reactions with rapid establishment of adsorption equilibrium and a linear adsorption isotherm.

The kinetics can be described approximately by the set of equations for steady-state operation of the reactor.

Before describing examples of the use of a microcatalytic reactor in investigating complicated catalytic reactions, let us consider briefly certain general aspects of the elucidation of formal kinetics from experimental data. Hitherto it has not been entirely clear [56-62] under what conditions all the paths of a complicated reaction can be determined with sufficient accuracy and the constants of individual transitions calculated from data obtained when all the processes in the system are occurring simultaneously. The main difficulty in the choice of the most probable mechanism for a complicated reaction is [58] that experimental errors do not permit differentiation between models yielding not greatly different calculated results. The position is considerably eased if statistical planning of the experiment [63] is used, but even then an unambiguous assessment of the adequacy of a model cannot always be expected.

The microcatalytic reactor has been used [64] to study the oxidative dehydrogenation of isopentenes to isoprene

$$2C_5H_{10} + O_2 \rightarrow 2C_5H_8 + 2H_2O \qquad (38)$$

on an iron–zinc–chromium oxide catalyst. The following assumptions were made on the basis of preliminary experiments and published information: (1) reaction (38) is irreversible, of first order with respect to the alkenes, and of zero order with respect to oxygen when it is in excess; (2) further oxidation to carbon monoxide and dioxide does not take place under the experimental conditions; and (3) isomerisation of the alkenes is described by a first-order equation. The above hypotheses are satisfied by the scheme in Fig. 6, which can be described by a linear set of equations.

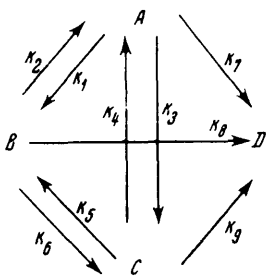


Figure 6. Scheme of interconversion in the oxidative dehydrogenation of isopentenes: A) 3-methylbut-1-ene; B) 2-methylbut-1-ene; C) 2-methylbut-2-ene; D) isoprene.

The initial rates wA, wB, wC, and wD were determined graphically [64] by differentiating the initial portions of the rate curves obtained for each set of compositions. Initial mixtures were prepared with compositions corresponding to the planning matrix of the complete factorial experiment [63]. Using as a first approximation the constants obtained by planning the experiment, more accurate values were found from the condition that differences between calculated and experimental partial pressures should be minimal. The values were refined from the experimental kinetic curves by the method of steepest descents [65]. This yielded for the rate constants (in s^{-1}) the values

$$k_5 = 12.8 \pm 0.4; \quad k_6 = 5.5 \pm 0.2;$$
$$k_7 = 0.7 \pm 0.2; \quad k_8 = 3.7 \pm 0.2;$$
$$k_9 = 1.1 \pm 0.1.$$

The values of k_1–k_4 in Ref. 64 were small. Since equating each of the constants to zero produced only an insignificant change in the calculated concentrations, it was impossible to determine their exact values. It was established, however, that $k_3 > k_1 > k_2 > k_4$. Additional kinetic experiments with the pure isomers were necessary in order to establish this sequence.

A microcatalytic reactor has been used also [66] to study the oxidative dehydrogenation of pentenes under conditions such that further oxidation of the pentenes and of isoprene also occurred. A set of differential equations was written on the above hypotheses that all reactions were of the first order, and these were solved by two methods—approximate integration by means of Simpson's formula [67] and numerical integration on an M20 computer—the rate constants being so chosen that concentrations calculated on the electronic computer approached as closely as possible to the experimental values. Good agreement was obtained between results obtained by the two methods.

VIII. USE OF MICROREACTOR AND RADIOCHROMATOGRAPHY FOR STUDY OF COMPLICATED CATALYTIC CONVERSIONS

Mathematical models evidently do not always give a clear and reliable criterion for distinguishing between particular schemes for a complicated process. The additional information usually employed for sifting certain hypothetical schemes is extremely useful. In order to select the most probable reaction scheme we must investigate the agreement between the chosen model and experiment with a wide variation in the experimental parameters. In this respect broad possibilities are opened up by combining the microcatalytic reactor with radiochromatography. The first attempt to do this was made in the fundamental work by Emmett and his coworkers [1]. However, these workers were unable to make any quantitative estimates of rates. Significant progress can be made by combining the microcatalytic reactor with the kinetic isotope method, which was suggested by Neiman more than fifteen years ago [68-70].

This latter combination of methods was first applied by Roginskii et al. [71-75] in studying the oxidative dehydrogenation of butenes to butadiene. The possible reactions can be represented by Fig. 7, in which [A]–[D] are the concentrations and α–δ the specific radioactivities of but-1-ene, *trans*-but-2-ene, *cis*-but-2-ene, and butadiene respectively. Three series of experiments were made by introducing into the microcatalytic reactor mixtures of two components of specified chemical and radiochemical composition—(I) butadiene + *cis*-[^{14}C]but-2-ene, (II) but-1-ene + *cis*-[^{14}C]but-2-ene, and (III) but-1-ene + *trans*-[^{14}C]but-2-ene—by the method of impinging pulses [75]. The concentrations of A–D and the specific radioactivities α–δ were determined by radiochromatographic analysis [76-78].

If all stages of the scheme had been reversible, the specific radioactivity of *trans*-but-2-ene would have been given by [70]

$$\frac{d\beta}{d\tau} = \frac{\delta-\beta}{[B]} w_{D-B} + \frac{(\gamma-\beta)}{[B]} w_{C-B} \frac{(\alpha-\beta)}{[B]} w_{A-B} \qquad (39)$$

where w_{D-B}, w_{C-D}, and w_{A-B} are the rates of conversion of butadiene, *cis*-but-2-ene, and but-1-ene respectively into *trans*-but-2-ene. Experiment showed that $d\beta/d\tau \simeq 0$. Further, it can be assumed with a certain approximation that $\gamma - \beta \simeq 0$ and $\alpha - \beta \simeq 0$. Since $\delta - \beta \neq 0$, Eqn. (39) is valid only when

$$w_{D-B} = 0;\ w_{D-A} = 0;\ w_{D-C} = 0$$

i.e. hardly any butene was formed from butadiene in the above experiments.

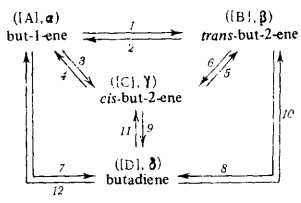


Figure 7.

Experiment showed that $w_{C-D} > w_{C-A}$. The variation in specific radioactivities found experimentally indicates that *trans*-but-2-ene and butadiene obtained from *cis*-[^{14}C]but-2-ene are diluted with but-2-ene and butadiene formed from but-1-ene:

$$\frac{d\beta}{d\tau} < 0 \qquad (40) \qquad\qquad \frac{d\delta}{d\tau} < 0 \qquad (41)$$

It was shown that butadiene was diluted considerably more strongly. Hence it follows that

$$w_{A-D} > w_{A-B}$$

Inspection of the curves obtained for series (III) indicated that the *cis* → *trans* isomerisation was more rapid than the reverse process:

$$w_{C-B} > w_{B-C} \qquad (42)$$

and also that

$$w_{C-D} > w_{B-D} \qquad (43)$$

Experiments were made with ternary systems (but-1-ene + *cis*-[^{14}C]but-2-ene + butadiene) in order to determine the immediate precursors of butadiene. The specific radioactivity of butadiene has a maximum value, which is lower than the specific activity of *cis*-[^{14}C]but-2-ene at time τ_{max}:

$$\delta_{\tau_{max}} < \gamma_{\tau_{max}} \qquad (44)$$

This implies that *cis*-but-2-ene is not the sole precursor of butadiene in the system. The ratio $\gamma\tau_{max}/\delta\tau_{max}$ indicated that the rate of formation of butadiene from but-1-ene was about double the rate from *cis*-but-2-ene:

$$w_{A-D} \approx 2w_{C-D} \qquad (45)$$

Radiochromatography has been combined with a microcatalytic reactor in order to estimate the six rate constants for the interconversion of but-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene on an aluminosilicate catalyst [79].

A microcatalytic reactor has been combined with radiochromatography to study the oxidative dehydrogenation of butenes on a bismuth–molybdenum catalyst, the results being processed on an electronic computer [80]. Finding the kinetic constants encountered considerable difficulty owing to the simultaneous occurrence under the experimental conditions of nine separate reactions of isomerisation and mild oxidation, as in the study of the oxidative dehydrogenation of isopentenes (Fig. 6). The kinetics of oxidative dehydrogenation could be represented by a set of differential equations. Statistical planning of experiments [63] and non-linear programming [81] were also used. The preliminary values of the constants calculated by this method were then refined [80] using Neiman's kinetic isotope method and a microcatalytic reactor.

Rate constants for the conversion of stable compounds are determined in the kinetic isotope method by the simultaneous solution of the material balance equations of the reactants in terms of concentration and radioactivity. If the complete reaction scheme has been chosen correctly, the rate constants obtained should describe accurately the variation in the specific activities of the products with time.

If the specific radioactivities of but-1-ene, *trans*-but-2-ene, *cis*-but-2-ene, and butadiene are denoted by α, β, γ, and δ (Fig. 7), it can be shown by Neiman's method that the variation in the specific radioactivities of these hydrocarbons is represented by the equations

$$\frac{d\alpha}{dt} = \frac{1}{[A]}\{k_4[C](\gamma - \alpha) + k_2[B](\beta - \alpha)\} \qquad (46)$$

$$\frac{d\beta}{dt} = \frac{1}{[B]}\{k_1[A](\alpha - \beta) + k_5[C](\gamma - \beta)\} \qquad (47)$$

$$\frac{d\gamma}{dt} = \frac{1}{[C]}\{k_3[A](\alpha - \gamma) + k_6[B](\beta - \gamma)\} \qquad (48)$$

$$\frac{d\delta}{dt} = \frac{1}{[D]}\{k_7[A](\alpha - \delta) + k_8[B](\beta - \delta) + k_9[C](\gamma - \delta)\} \qquad (49)$$

Comparison of experimental and calculated specific radioactivities of products of oxidative dehydrogenation at 396°C (for the series but-1-ene + *cis*-[^{14}C]but-2-ene).

Time of contact, s	But-1-ene		*trans*-But-2-ene		*cis*-But-2-ene		Butadiene	
	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
0.0065	9.4	9.4	92.0	92.0	155	155	20.0	20.0
0.0090	11.0	12.7	93.0	93.0	151	152	30.0	32.8
0.0118	15.0	16.3	94.0	95.2	149	149	39.0	42.8
0.0144	17.5	19.5	94.5	97.0	145	146	48.0	50
0.0190	23.0	25.0	96.0	98.0	140	141	58.5	59.6

These were solved together with the equations of material balance, and the rate constants were calculated with an electronic computer from the condition that the calculated curves for the variation in concentrations and specific activities with time should be close to the experimental curves. The Table shows agreement between experimental and calculated values of the specific activities of the components for various contact times.

Rate constants determined by means of a microcatalytic reactor combined with Neiman's kinetic isotope method were given [80] for the individual reaction paths in the oxidative dehydrogenation of butenes to butadiene. The dehydrogenation of but-1-ene was the most rapid (especially at low temperatures). At high temperatures the oxidative dehydrogenation of *cis*- and *trans*-but-2-enes also becomes appreciable.

A promising approach was shown [80] for combining computer processing of kinetic curves obtained by means of a microcatalytic reactor with continuous checking of the results by radiochromatography. This makes calculation of the constants less formal, and also reduces considerably the volume of laborious and complicated isotopic experiments.

IX. PULSE METHOD FOR STUDY OF POISONING OF CATALYSTS

The poisoning of catalysts by various poisons is usually studied with the aim of obtaining information on the number and nature of the active centres. Pulse methods have recently begun to be used to study poisoning [82,83]. This usually involves introducing, into a stream of an inert carrier gas entering the reactor at the reaction temperature, a fixed dose of the poison, which is adsorbed on the catalyst surface. After this the activity of the poisoned catalyst is studied, also by a pulse method. This method of study was probably first applied to the dehydrogenation of butane to butenes and butadiene [7]. Turkevich et al. [82] introduced several successive doses of the poison into the reactor in order to study the dependence of the activity of the catalyst on the dose. However, it then emerged [83] that under pulse conditions catalyst poisoning is a transient process, and therefore irreproducible results may be obtained. The method was subsequently developed by Romanovskii, Topchieva, and their coworkers [83-85].

Until recently no theoretical examination had been made of poisoning in a pulse reactor. Romanovskii [86] pointed out that, for non-linear laws of poisoning, not only the quantity of poison absorbed by the catalyst surface but also its distribution along the bed are significant.

A quantitative theory of the pulse poisoning of catalysts has recently been developed [87,88] taking into account the adsorption characteristics of the poison. Two types of centres are supposed to be present on the catalyst surface. A first-order heterogeneous catalytic reaction takes place on the first group of centres; the starting material may be adsorbed reversibly on the second group, but this does not involve any reaction. It is assumed also that the poison is adsorbed considerably more firmly than the initial substance, and that adsorption of the poison is described by the Langmuir equation.

On the basis of the above model, equations were obtained for the time variation of catalytic activity after introduction of the poison. With reversible adsorption of the poison, the activity of the catalyst first falls, reaches a minimum value, and then gradually increases to the original level. The initial fall in catalytic activity is due to the fact that the poison is located entirely on the catalyst bed. The chromatographic band of the poison is blurred, and its molecules are redistributed between catalytic and adsorption centres. When the poison band reaches the outlet from the reactor, the activity of the catalyst increases, to reach its original value when the last poison molecules leave the reactor.

With an exponential law of poisoning the descending portions of the curves can be represented by the equation

$$\frac{A_g}{A_0} = y + 1 - (\sqrt{\mu} + \sqrt{y})^2 + \int_{y}^{(\sqrt{\mu}+\sqrt{y})^2} \exp - \nu_k \frac{\beta\left(\sqrt{\frac{z}{y}} - 1\right)}{1 + \beta\left(\sqrt{\frac{z}{y}} - 1\right)} dz \qquad (50)$$

and the ascending portions by the formula

$$\frac{A_g}{A_0} = y + \int_{y}^{1} \exp - \nu_k \frac{\beta\left(\sqrt{\frac{z}{y}} - 1\right)}{1 + \beta\left(\sqrt{\frac{z}{y}} - 1\right)} dz \qquad (51)$$

where $A_0 = \lg(1 - \alpha_0)^{-1}$ is the initial activity of the catalyst, α_0 the degree of conversion of the reactant before introduction of the poison, A_g the activity of the poisoned catalyst, $y = t/t_{max}$ the dimensionless time, t the time, t_{max} the time of complete regeneration of the catalyst, $\mu = m_0/q_{max}$ the reduced dose of poison, m_0 the quantity of poison introduced into the reactor, q_{max} the quantity of poison required for a monolayer, b_K the adsorption coefficient of the poison on the active centres, b the mean adsorption coefficient of the poison on catalytic and adsorption centres, and ν_K the number of poison molecules which can be adsorbed on one active centre in the catalyst surface.

The position of the minimum y_{min} in the experimental dependence of the relative activity of the catalyst on the dimensionless time can be used to determine q_{max}:

$$q_{max} = \frac{m_0}{(1 - \sqrt{y_{min}})^2} \qquad (52)$$

The mean adsorption coefficient of the poison b is determined from the time of complete regeneration of the catalyst:

$$b = \frac{v \cdot t_{max}}{q_{max}} \qquad (53)$$

where v is the space velocity of the carrier gas. Furthermore, the most probable law of poisoning can be selected from a comparison of calculated and experimental results, and the ratio of the adsorption coefficients β determined. The adsorption coefficient of the poison on the active centres is then found from the simple relation

$$b_k = b\beta \qquad (54)$$

The above theory of pulse poisoning has been verified in a study [88] of the poisoning by pyridine of an aluminosilicate catalyst for the cracking of cumene. Values of b and q_{max} calculated from the time variation of activity during poisoning were compared with direct measurement of the adsorption of the poison on the catalyst under the same conditions. Satisfactory agreement was obtained.

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The information reviewed above shows that the pulse chromatographic method can be successfully applied to the solution of many problems in the field of catalysis. The range of application of the method has been continuously extended as the theory of the method has been improved. It must be borne in mind, however, that, since the method is transient, difficulties inevitably arise in processing the measurements, especially in the case of non-linear adsorption isotherms.

An attempt to avoid these difficulties led to a second form of the pulse method, in which a broad rectangular pulse, whose front and rear edges are as sharp as possible, is introduced into a relatively small reactor [89]. The idea is that, by introducing a "wide" pulse, it can be assumed that adsorption–chemical equilibrium is established, and the process can be regarded as stationary–microdynamic.

The results can now be processed by methods adopted in work with a flow-type reactor. When the properties of the catalyst vary slowly with time, it is possible to examine the effect of the reaction medium on the properties of the active surface. A weak point in the method is some arbitrariness in the choice of pulse width, which must correspond to the rate of establishment of adsorption–chemical equilibrium. However, it is not always a simple matter to estimate the rate of adsorption and desorption during catalysis. In particular, such a method may lead to errors in the case of slow irreversible chemisorption on the layer of catalyst. It must be remembered that the use of wide pulses is suitable mainly in work with low concentrations of the starting material, since, when a wide pulse with a high partial pressure of the starting material is introduced into the microreactor, it can no longer be always assumed that the properties of the catalytic surface remain unchanged during passage of the pulse along the catalyst bed.

A significant advance is the recently proposed[90] gradient free pulse method, in which the pulse of reactant is introduced into a microreactor containing a pseudo-fluidised bed of the catalyst. This has the advantage over the preceding method that, because of the absence of gradients, the reaction velocity can be measured directly under specified experimental conditions. However, this method is not free from the defects inherent in the above "microdynamic method"—those involving the choice of sample size and the need to work with low concentrations of the starting material.

In the present paper we have wanted to show that the theory of transient processes occurring under pulse conditions has recently been undergoing vigorous development. Such development has been stimulated by the great opportunities for pulse methods in the study of the kinetics and the mechanism of transient processes.

The chromatographic technique will yield information which it is sometimes impossible to obtain by traditional methods. In our opinion it is not necessary to strive to replace stationary by pulse methods. These methods should be used to solve different problems, supplementing each other.

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