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Kinetics of Homogeneous Reactions in Reaction Vessels with Ideal Mixing (Open Systems)

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The main kinetic features of chemical reactions occurring in flow systems with complete mixing are surveyed. The advantages are discussed of conducting a reaction in a flow system with stirring as compared with reactions under static conditions in a laminar flow. Considerable attention is paid to the establishment of oscillatory (pulsating) régimes. The dependence of the steady-state concentrations on the reaction conditions is examined, as also the kinetics of the establishment of a steady-state. A considerable part of the review is devoted to investigating the possibilities presented by open systems for studying the mechanism of chemical reactions and determining the rate constants of individual elementary stages in complicated chain processes. A list of 70 references is included.

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I. INTRODUCTION

Investigations of the kinetics of reactions in open systems, with continuous supply of the starting materials and withdrawal of the reaction products, arouse great interest in connection with the opportunities created for studying the mechanism of chemical reactions. These investigations are also of fundamental value because data on the mechanism and kinetics of reactions occurring in an open system are necessary for the design of present-day automatically controlled technical processes.

When a process is conducted under static conditions, certain quantities of starting materials are introduced into the system, and then undergo several chemical changes. In this case both the starting materials and the reaction products remain within the system: i.e. they do not leave

the reaction zone. The process is complete in a time determined by the quantity of starting materials taken and the rate constants of their conversion. The steady state, which is reached in some cases, represents the establishment of thermodynamic equilibrium. In an open system the unlimited supply and withdrawal of all the components of the reaction make it possible to establish a steady state differing from the thermodynamic equilibrium and characteristic not only for reversible but also for unidirectional reactions.

Processes with continuous supply and withdrawal of reactants can be conducted in two fundamentally different ways—under conditions of ideal (or complete) displacement and under conditions of ideal (complete) mixing†.

A vessel having ideal displacement is a reaction vessel into which a mixture of the reactants is introduced, and the reaction mixture is removed when a particular degree of conversion has occurred. Diffusion of the reactants in a vessel of ideal displacement should be reduced to a minimum. The composition of the reaction mixture in a given element of volume is determined solely by the extent of chemical reaction and varies along the length of the vessel. The residence time of all species in the reaction zone (the "contact time") is the same. Henceforward reactions occurring in vessels with ideal displacement will be termed "reactions in a flow".

The study of reactions in a flow is greatly complicated at high temperatures by convection currents and the presence of temperature gradients.

The second type of reaction vessel for conducting a reaction in a flow system is a "vessel with ideal mixing" (a "gradient-free reaction vessel"). In a vessel with ideal mixing the composition of the reaction products at a given time should be kept uniform throughout the volume by diffusion or by special mixing of freshly arriving substances with the partly reacted mixture. Such systems are also termed "open systems", since, in contrast to reactions in a streamlined flow, any given element of volume of the reaction mixture is "open" to freshly arriving substances. Change in the composition of the reaction mixture occurs not only as a consequence of chemical reaction but also as a result of the additional introduction of starting materials and reaction products from adjacent volumes. The residence times of species in the vessel are not the same. The mean residence time τ of species in the reaction volume is taken to be the reciprocal of the rate of supply of the starting materials to unit volume: i.e. $\tau = V/u$, where V is the volume of the reaction vessel and u the volume rate of supply of the reactants.

Both principles of an unenclosed system—reaction vessels of ideal displacement and of ideal mixing—are used in chemical technology. The latter are employed particularly in heterogeneous catalytic reactions and in other reactions involving solid particles, occurring in a "fluidised bed".

Several other chemical reactions can be more suitably conducted either in a laminar flow or with some definite degree of diffusion, which eliminates laminarity but does not guarantee complete mixing. However, it is fairly difficult to achieve conditions of complete laminarity and especially of a specified degree of diffusion, and in some cases, therefore, it is preferable to conduct the processes in several reaction vessels of ideal mixing connected in series.

† There may also be intermediate types of reaction vessels, with breakdown of laminar flow but not complete mixing.

To study reaction mechanisms it is also more convenient to use a "gradient-free reaction vessel", since the study of reactions in a streamlined flow requires either the careful elimination of or allowance for diffusion, the latter leading to rather unwieldy equations, which cannot be integrated in quadratures even for simple types of reactions.

The use of flow systems with complete mixing to investigate the kinetics of chemical reactions was initiated in 1905 by Bodenstein's work[1] on the kinetics of the reaction $H_2 + I_2 \rightleftharpoons 2HI$.

Conducting a reaction in a gradient-free reaction vessel enables the set of differential equations to be reduced to a set of algebraic equations, which considerably simplifies the task of determining the rate constants of complicated reactions.

Conducting a process in an open system has a further advantage over reactions under static conditions and in a laminar flow: it becomes possible to study processes over a considerably wider temperature range, since the continuous supply of starting materials to the system eliminates the possibility of the starting materials being completely burned up.

The present review will give an account of the main kinetic laws of homogeneous reactions occurring under conditions ensuring complete mixing with continuous supply and removal of substances to and from the reaction zone. We shall not discuss the kinetics of the series of heterogeneous processes in a flow examined in the works of Boreskov, Slin'ko, Temkin, Ioffe, Panchenkov, Nagiev, and other authors[2-6].

II. STEADY STATE IN AN OPEN SYSTEM

Various types of reaction vessel, with and without stirrers, can be used[7,8] to investigate homogeneous reactions in a flow with complete mixing, depending on the type of reaction and the necessary range of variation in flow rates.

For very rapid processes the completeness of mixing can be judged from the kinetics of the accumulation of reaction products being independent of the rate of mixing. With slower processes a method can be employed[9,10] in which a solution of a substance A, which undergoes no chemical change under the experimental conditions, is fed at a constant rate into a vessel filled with the pure solvent. The kinetics of the accumulation of this substance in the system will be described by the differential equation

$$\frac{d(a/a_0)}{dt} = \frac{u}{V} - \frac{u}{V}\left(\frac{a}{a_0}\right) \qquad (1)$$

where a_0 is the concentration of A in the solution fed into the vessel, u the volume flow rate, and V the volume of the system. Integration of Eqn. (1) yields

$$\ln\left(\frac{a_0}{a} - 1\right) = -\frac{u}{V} \cdot t \qquad (1a)$$

which describes the kinetics of the accumulation of A in the system. The slope of the semilogarithmic plot of $\ln[(a_0/a) - 1]$ against t will give the specific rate of supply of the starting materials to the system. Agreement between the experimental value of u/V and the value calculated from the known volume of the reaction vessel and the bulk rate of supply of A to the system indicates that mixing is complete in the vessel.

If a reaction occurring in an open system involves no change in volume, the concentrations both of the starting materials and of all intermediate and final products of the reaction will cease to change some time after the start of

the process: i.e. steady-state concentrations of all the components of the reaction are reached‡. A steady state can be defined as a state in which it is impossible to distinguish any macroscopic changes in the system[11]. Under these conditions the sum of the rates of formation of a product and of its supply to the reaction vessel is equal to the sum of its rates of consumption and removal from the reaction zone.

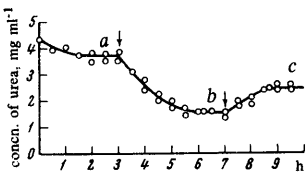


Figure 1. Steady-state concentrations of urea during its decomposition: a) in absence of an enzyme; b) in the presence of additions of an enzyme; c) on deactivation of the enzyme by $AgNO_3$ solution.

Establishment of a steady state in an open system has been observed with several simple and complicated reactions. Examples are the inversion of cane-sugar[9], the initiated polymerisation of styrene[12], the enzymic decomposition of urea[13] (Fig. 1), the decomposition of potassium persulphate catalysed by sulphuric acid[14], and the autoxidation of several hydrocarbons and their derivatives[15-17] (Fig. 2).

1. Time of Establishment of Steady State

If the concentration of a reaction product is zero at the start of a continuous process, the time of establishment of a steady state will depend solely on the rate of supply of the starting materials and the rate constants of the process[14]. The time for establishment of steady-state concentrations of the starting materials will differ from the corresponding time for the reaction products.

Let us examine the kinetics of the establishment of steady-state concentrations of starting material and reaction product in the case of a simple first-order reaction $A \xrightarrow{k_1} B$. The rate of consumption of the starting material A in the system is

$$\frac{da}{dt} = -\left(k_1 + \frac{u}{V}\right) a + \frac{u}{V} a_0.$$

Solution of this equation with the initial conditions $a = 0$ at $t = 0$ yields

$$-(k_1 + u/V)t = \ln \frac{(u/V)\,a_0 - (k_1 + u/V)\,a}{(u/V)\,a_0} = \ln\left(1 - \frac{a}{\bar{a}}\right) = \ln(1 - \alpha) \quad (2)$$

where α is the degree of conversion and $\bar{a} = a_0 u/V[k_1 + (u/V)]$ is the steady-state concentration of A. It is seen that the time required to reach any given degree of conversion (e.g. $a = 0.99\bar{a}$, where $\bar{a}$ is the steady-state concentration) depends on the rate of flow and the rate constant k_1:

$$t_{99\%} = \frac{4.6}{k_1 + u/V}. \quad (3)$$

Conversion to 50% of the steady-state value is achieved at

$$t_{50\%} = \frac{0.639}{k_1 + u/V}. \quad (3a)$$

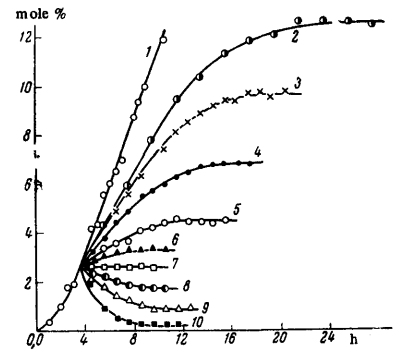


Figure 2. Kinetic curves for the accumulation of adipic acid by the oxidation of cyclohexanone in a reaction vessel of ideal mixing at 110°C with various rates of flow (h^{-1}): 1) 0; 2) 0.04; 3) 0.08; 4) 0.118; 5) 0.24; 6) 0.35; 7) 0.47; 8) 0.55; 9) 0.79; 10) 1.18.

We may note here that, when a first-order reaction is carried out in an open system, the time required to reach a definite degree of conversion of the starting material ($a = \alpha\bar{a}$) is independent of the concentration of A in the solution supplied to the vessel. This is analogous to the fact that under static conditions the time for a definite percentage conversion of the starting material to be achieved is independent of its initial concentration, being determined solely by the rate constant of the process.

The rate of accumulation of the final product B in a first-order reaction is given by the differential equation

$$\frac{db}{dt} = k_1 a - \frac{u}{V} b.$$

In this case

$$1 - \frac{b}{\bar{b}} = e^{-(u/V)\cdot t} - \frac{u}{Vk_1} e^{-(k_1 + u/V)t}. \quad (4)$$

When a steady-state concentration of A ($a = 0.99\bar{a}$) is reached with $u/V = k_1$, we have $1 - (b/\bar{b}) = 0.09$: i.e. the steady-state concentration ($b = 0.99\bar{b}$) will not yet have been reached. Calculation based on Eqn. (4) with $u/V \simeq k_1$ shows that the time required for a steady-state concentration of the product B to be established will be approximately double the time required to reach a steady-state concentration of the starting material A.

For a reaction A + B → F with a rate constant of 0.002 M^{-1} min^{-1}, the time required for establishment of the steady-state concentration of a starting material has been shown to be 4τ, and that for the reaction product 6τ (calculations approximate to 1%).[12]

‡ If the system undergoes a change in volume, steady-state concentrations may not be achieved.

In the case of the polymerisation of styrene in the presence of benzoyl peroxide it has been found[12] that a steady-state concentration of styrene is reached in a time 7τ which is independent of the order of the reaction (the order may vary during the process and with different initial conditions). The calculations were based on the known rate constant for the consumption of styrene during polymerisation at 80°C.

2. Kinetics of Establishment of Steady State

The transition from one steady state to another with change in the conditions under which the process is occurring is of considerable interest. It is found that in several cases such transitions are not accomplished monotonically[8,13,14,18,19]: before the new steady state is reached the concentrations of the substances may pass through a maximum or a minimum. Two different phenomena are possible (see Fig. 3).

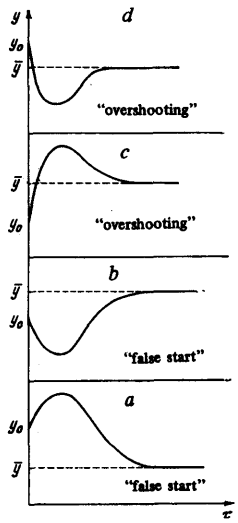


Figure 3. Diagrammatic representations of "overshooting" and "false start" phenomena when a reaction occurs in a vessel of ideal mixing.

1. In the phenomenon of the "false start" an initial change in some parameter of the system is immediately followed by a change in the concentration of the product in the opposite direction to that of the new steady-state concentration. Thus if the initial steady-state concentration of a substance A is a_0, and its new steady-state concentration a_1, a "false start" will give $(da/dt)_{t=t_0} < 0$ when $a_0 - a_1 < 0$ (a minimum is observed on the curve), or $(da/dt)_{t=t_0} > 0$ when $a_0 - a_1 > 0$ (a maximum is observed on the curve).

2. In the "overshooting" phenomenon the initial change in the concentration of a substance is towards the new steady-state concentration: with $a_0 - a_1 < 0$ we have $(da/dt)_{t=t_0} > 0$, and with $a_0 - a_1 > 0$ the derivative $(da/dt)_{t=t_0} < 0$. At a certain time the concentration of the reaction product exceeds the steady-state value (or is lower than the latter), and only by passing through a maximum (or minimum) is the steady-state value reached.

The conditions under which a "false start" or "overshooting" occurs have been determined for a first-order reversible reaction $A \rightleftharpoons B$ and the consecutive reaction $A \rightarrow B \rightarrow C$ when the rates of supply of starting material and of removal of reaction products differ greatly[14] and also when they are the same[8].

Let us examine in rather greater detail the possibility of the occurrence of a "false start" and "overshooting" on the kinetic curves for the accumulation of reaction products in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ with identical rates of supply and removal of all products[8]. In this case, denoting the concentrations of A and B by x and y, we can write down the set of differential equations

$$\frac{dx}{dt} = -(k_1 + u/V)\,x + \frac{u}{V}\tilde{x}_0 \qquad (5)$$

where $\tilde{x}_0$ is the concentration of the component A in the solution fed to the vessel, and

$$\frac{dy}{dt} = k_1 x - (k_2 + u/V)\,y\,. \qquad (6)$$

Introducing the new variables $\Delta x = x - \bar{x}$ and $\Delta y = y - \bar{y}$ (where $\bar{x}$ and $\bar{y}$ are the steady-state concentrations of A and B respectively), and remembering that

$$\frac{d\bar{x}}{dt} = -(k_1 + u/V)\,\bar{x} + \frac{u}{V}\tilde{x}_0 = 0 \qquad \frac{d\bar{y}}{dt} = k_1\bar{x} - (k_2 + u/V)\,\bar{y} = 0$$

we can reduce the differential equations (5) and (6) to the form

$$\frac{d\Delta x}{dt} = -(k_1 + u/V)\,\Delta x \qquad (7)$$

$$\frac{d\Delta y}{dt} = k_1\Delta x - (k_2 + u/V)\,\Delta y. \qquad (8)$$

Integration of (7) and (8) will give

$$\Delta x = \Delta x_0 e^{-(k_1+u/V)(t-t_0)}$$

$$\Delta y = \frac{k_1\Delta x_0}{k_2-k_1}\{e^{-(k_1+u/V)(t-t_0)} - e^{-(k_2+u/V)(t-t_0)}\} + \Delta y_0 e^{-(k_2+u/V)(t-t_0)}$$

where $\Delta x_0 = x_0 - \bar{x}$ and $\Delta y_0 = y_0 - \bar{y}$ are the deviations in the concentrations x and y in the system from the steady-state values at $t = t_0$ (where t_0 corresponds to the instant of transition from the continuous régime, change in the rate of flow, etc.).

The derivative

$$\frac{d\Delta y}{dt} = (k_2 + u/V)\left[\frac{k_1\Delta x_0}{k_2-k_1} - \Delta y_0\right] e^{-(k_2+u/V)(t-t_0)} - \frac{k_1\Delta x_0}{k_2-k_1} e^{-(k_1+u/V)(t-t_0)}$$

can vanish as $t \to \infty$, which corresponds to the establishment of a steady state, and also when

$$(t-t_0) = \frac{1}{k_2-k_1}\ln\left\{\left[1 - \frac{\Delta y_0\,(k_2-k_1)}{k_1\Delta x_0}\right]\frac{k_1+u/V}{k_2+u/V}\right\}. \qquad (9)$$

If Eqn. (9) is satisfied, extremal values appear on the kinetic curves for accumulation of the intermediate substance.

Analysis of Eqn. (9) together with the differential equation (8) will give the following conditions for the appearance of "overshooting" and a "false start" on the kinetic curve for the accumulation of the intermediate B in the above consecutive reaction[8].

1. If $\Delta x_0 > 0$ and $\Delta y_0 > 0$ at zero time, a "false start" with a maximum on the curve may be observed at values of $u/V < (k_1\Delta x_0/\Delta y_0) - k_2$.

2. With $\Delta x_0 < 0$ and $\Delta y_0 < 0$ a "false start" with a minimum may be observed at velocities

$$u/V < \frac{k_1 \Delta x_0}{\Delta y_0} - k_2 .$$

3. When $\Delta x_0 > 0$ and $\Delta y_0 < 0$ "overshooting" with a maximum can be observed throughout the range of variation in u/V, and when $\Delta x_0 < 0$ and $\Delta y_0 > 0$ "overshooting" with a minimum on the kinetic curve can occur.

The phenomena of a "false start" and "overshooting" have been observed experimentally in particular on the kinetic curve for the accumulation of sulphuric acid (the final product of the decomposition of potassium persulphate (Fig. 4*a*) accompanied by the liberation of atomic oxygen[14])

$$K_2S_2O_8 + H_2O \rightarrow K_2SO_4 + H_2SO_4 + O$$

and also in the enzymic decomposition of urea in the presence of urease and additions of silver nitrate, causing inactivation of the enzyme[13], as well as in the complicated chain oxidations of n-decane and ethylbenzene by atmospheric oxygen (Fig. 4*b*).[8]

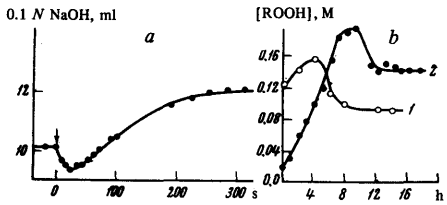


Figure 4. (a) "False start" on kinetic curve for accumulation of sulphuric acid during decomposition of aqueous potassium persulphate solution in reaction vessel of ideal mixing. The arrow indicates the instant at which the rate of diffusion changes. (b) Kinetic curves for accumulation of hydroperoxides in the oxidation of n-decane in a reaction vessel of ideal mixing at 140°C: 1) "false start"; 2) "overshooting".

The possibility of the appearance of "overshooting" and "false starts" on kinetic curves for the consumption of starting material in an open system has been examined in a previous paper[20]. If the reaction is of the first order (see above) the derivative

$$-\frac{d\Delta x}{dt} = \Delta x_0 (k_1 + u/V) e^{-(k_1 + u/V)(t - t_0)}$$

is able to vanish only at $t = t_\infty$, i.e. in a steady state. At all values of $t \neq t_\infty$ the concentration of the starting material either increases monotonically when $\Delta x_0 < 0$ or falls monotonically when $\Delta x_0 > 0$. Consequently the concentration of the initial reactant can only vary monotonically on passing from one stationary state to another: the occurrence of any extrema is then impossible. This holds for a non-autocatalytic reaction of any order[20].

In fact, for a reaction of the nth order we have

$$\frac{d[A]}{dt} = -k_1 [A]^n - (u/V)[A] + (u/V)[A]_0$$

and when $d[A]/dt = 0$ the second derivative

$$\frac{d^2[A]}{dt^2} = [-k_1 n [A]^{n-1} - u/V] \frac{d[A]}{dt} \equiv 0$$

which corresponds to the establishment of a steady state. Thus the kinetic curve for the consumption of A cannot pass through extrema.

In autocatalytic reactions, unlike those of simple types, "overshooting" and "false start" phenomena can be observed even on the kinetic curves for the consumption of the starting material[20]. Actually, if the starting material A is consumed autocatalytically by interacting with the reaction product B, its rate of accumulation in the system is described by the differential equation

$$\frac{d[A]}{dt} = -k_1 [A][B] - \frac{u}{V}[A] + \frac{u}{V}[A]_0 .$$

At the instant at which $d[A]/dt = 0$ the second derivative

$$\frac{d^2[A]}{dt^2} = -k_1 [A] \frac{d[B]}{dt} - \left[k_1 [B] + \frac{u}{V}\right] \frac{d[A]}{dt}$$

may differ from zero if at this instant $d[B]/dt \neq 0$. In this case the kinetic curve for consumption of A will pass through a maximum or a minimum before a steady state is attained.

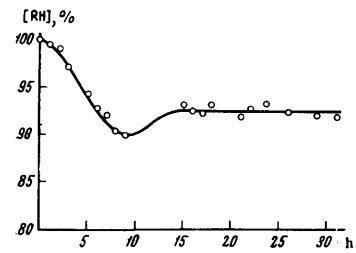


Figure 5. "Overshooting" on kinetic curve for consumption of ethylbenzene by oxidation in an open system at 118°C with a rate of flow of 0.102 h^{-1}.

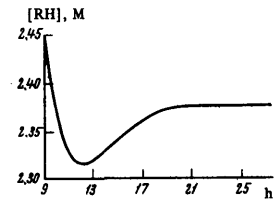


Figure 6. Kinetic curve for consumption of starting material in catalysed oxidation, calculated on M-20 electronic computer with [RH] = 5.2 M, [$CoSt_2$] = 0.006 M, and $u/V = 5 \times 10^{-5}$ s^{-1}.

The phenomenon of "overshooting" has been observed, for example, on the kinetic curve for the consumption of ethylbenzene during its autoxidation by oxygen (Fig. 5).[10]

The possibility of the appearance of extrema on kinetic curves for the consumption of the starting material has been shown also in the catalysed oxidation of hydrocarbons

in the presence of cobalt stearate[21]. The mechanism of the process in this case is represented by the scheme

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \quad (k_1)$$

$$ROOH + CoSt_2 \rightleftarrows ROOH \cdot CoSt_2 \quad (k_2,\ k_3)$$

$$ROOH \cdot CoSt_2 + CoSt_2 \rightarrow RO^{\cdot} + Co(OH)St_2 + CoSt_2 \quad (k_4)$$

$$ROOH + Co(OH)St_2 \rightarrow CoSt_2 + H_2O + RO_2^{\cdot} \quad (k_5)$$

In an open system the oscillations are maintained indefinitely. When malonic acid was replaced by malic acid, for example, oscillation at two frequencies was observed[29] under certain conditions (Fig. 8).

The very fact that periodic chemical reactions can occur is very interesting from the points of view both of chemical kinetics and of biology. Among the clearest periodic processes in biology are the biological systems for recording

The dependence of the steady-state concentration of radicals $\bar{n}$ on the initial concentration of inhibitor i_0 is found by solving the cubic equation

$$\bar{n}^3 - \frac{1}{k_6}\left(\frac{2k_2k_3[RH]}{(k_3 + u/V)} - \frac{u}{V} - \frac{uk_5}{Vk_i}\right)\bar{n}^2 + \\ + \frac{u}{Vk_6k_i}\left(k_i \cdot i_0 - \frac{2k_2k_3[RH]}{(k_3 + u/V)} + \frac{u}{V} - \frac{w_0k_i \cdot V}{u}\right)\bar{n} - \frac{u \cdot w_0}{Vk_ik_6} = 0 . \quad (11)$$

Equation (11) has three positive roots $\bar{n}_1$, $\bar{n}_2$, $\bar{n}_3$ (three steady states of the process) provided that

$$\frac{V}{u}\left[\frac{2k_2k_3[RH]}{(k_3 + u/V)} - \frac{u}{V}\right] > \frac{k_5}{k_i} .$$

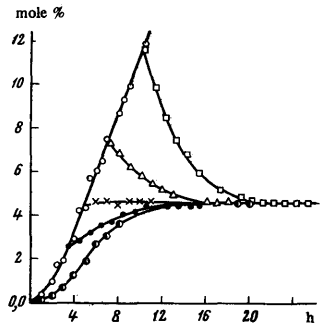


Figure 9. Kinetic curves for the accumulation of adipic acid during the continuous oxidation of cyclohexanone at 110°C with a rate of flow of 0.265 h^{-1}.

However, analysis shows that one of the solutions is unstable. The dependence of the steady-state concentration of the primary intermediate product, the hydroperoxide ROOH (the concentration of hydroperoxide is proportional to the concentration of radicals n), on the initial concentration of the inhibitor[42] is shown graphically[44] in Fig. 10. The section afb corresponds to the steady state $\bar{n}_1$, and the section cd determines $\bar{n}_3$. The state $\bar{n}_2$ (branch blc) is unsteady and is not realised.

Experimental data on the dependence of the steady-state concentration of a reaction product on the initial conditions have been obtained in an investigation of the inhibited oxidation of n-decane[42]. The steady-state hydroperoxide concentration is found to depend on the initial concentration

with change in the inhibitor concentration right until the latter corresponds to point b. At this inhibitor concentration the steady state of the system changes in the direction indicated by the arrow. Thus it is seen that, with the same inhibitor concentration in the solution fed to the vessel and different initial hydroperoxide concentrations in the system ($[ROOH]_0$ = 1.2 mole % and 0), two markedly different steady states are attained. The broken section b–c defines the magnitude of the unstable steady state. In the oxidation of n-decane containing hydroperoxide from the start, breaks are observed close to the critical inhibitor concentration on the kinetic curve of the hydroperoxide (sections a–b on the curves in Fig. 12).[42]

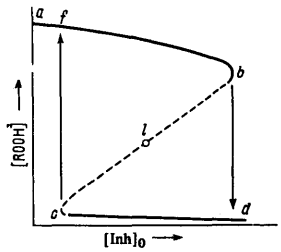


Figure 10. Dependence of steady-state concentration of hydroperoxide on initial concentration of inhibitor in a continuous process of oxidation (calculated results).

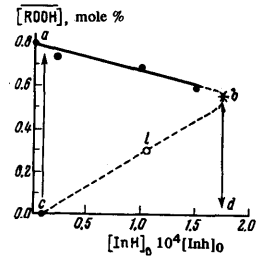


Figure 11. Dependence of steady-state concentration of hydroperoxide on concentration of 1-naphthol and initial hydroperoxide concentration in the system during the oxidation of n-decane with continuous supply of a solution of 1-naphthol in n-decane, at 135°C with rate of flow 1.45×10^{-4} s^{-1}.

With certain initial conditions[34] auto-oscillations can be expected also in a first-order exothermic reaction A → B under non-isothermal conditions.

Auto-oscillations can occur when the process can be described by a set of non-linear differential equations.

The possibility of the occurrence of oscillations has since been discussed theoretically for a large number of systems. In particular, detailed analysis has shown[35-37] that oscillations are impossible under isothermal conditions in systems in which only simple types of reactions take place. Only the presence of an autocatalytic stage or of a wall reaction can lead to the appearance of oscillations[37].

In the system

$$A_1 + M_1 \rightarrow M_2 + B_1$$
$$A_2 + M_2 \rightarrow M_3 + B_2$$
$$A_3 + M_3 \rightarrow M_1 + B_3$$

where the M_i are catalysts, damped and undamped oscillations are possible if the number of components in the reaction exceeds 3.

The occurrence of oscillations about a steady-state value has been discussed in detail for a consecutive reaction comprising n stages, all of which are autocatalytic, taking place in an open system[38]. It is shown that harmonic oscillations about a steady-state value should be observed if the number of consecutive stages does not exceed 3. If the number of stages does exceed 3, anharmonic oscillations are produced owing to the superposition of oscillations. The occurrence of oscillations, and also their frequency and amplitude, depend on the rate of supply of the starting materials to the system and on the initial conditions.

A detailed discussion of oscillatory phenomena in chemical and biological systems will be found in Ref. 39.

IV. DEPENDENCE OF STEADY-STATE CONCENTRATION ON CONDITIONS OF PROCESS

The steady-state concentration is determined by the parameters of the system (temperature, pressure, presence of a catalyst or an inhibitor, and also the rate of flow).

The change in the steady state produced by addition of a catalyst to a system has been shown, for example, in the enzymic decomposition of urea[13] and the decomposition of aqueous potassium persulphate solutions catalysed by silver sulphate[14]. It was shown in the former case[13] that different steady-state concentrations of urea are established in the system depending on the degree of inactivation of the enzyme by silver nitrate solution (Fig. 1). In the decomposition of potassium persulphate in aqueous solutions a change in the steady-state concentration of sulphuric acid (a reaction product) has also been observed on the addition of a catalyst (silver sulphate) to the system[14].

It is interesting that, if a reversible reaction is taking place in an open system, addition of a catalyst not only increases the rate of establishment of equilibrium, as occurs in a closed system, but also leads to a shift in the thermodynamic equilibrium[13a]. This phenomenon has been investigated theoretically[13a] for the first-order reversible reaction A ⇌ B.

Variation in temperature also influences the steady-state concentrations in a system. For example, the mean degree of vinyl polymerisation falls with rise in temperature[40] (this parameter is a function of the concentration of the monomer).

1. Dependence of Steady-State Concentration on Initial Conditions

For most reactions, having highly diverse mechanisms, the steady-state concentration under gradient-free conditions is independent of the concentration of products in the system at the instant of transition to a continuous régime. In the simplest case, when a substance A is consumed by a first-order reaction having a rate constant k_1, we have for the rate of the process the equation

$$\frac{da}{dt} = -(k_1 + u/V)a + (u/V)a_0 . \qquad (10)$$

Integration gives

$$-(k_1 + u/V)a + (u/V)a_0 = [(u/V)a_0 - (k_1 + u/V)a_1]e^{(k_1+u/V)t}$$

where a_1 is the concentration of A in the vessel at time $t = 0$. As $t \rightarrow \infty$ a concentration $\bar{a}$ is reached, which remains unchanged with time (steady-state concentration), and is given by

$$\bar{a} = \frac{(u/V)a_0}{(k_1+u/V)} .$$

This is independent of a_1, and is determined by the values of k_1 and u/V.

The same formula for $\bar{a}$ can be obtained by equating the derivative da/dt in Eqn. (10) to zero.

More generally we can write for the accumulation in an open system of a substance X, formed at a rate w_f and consumed at a rate w_u, the equation

$$\frac{dx}{dt} = w_f - w_u + (u/V)x_f - (u/V)x .$$

In this case the steady-state concentration $\bar{x}$ (determined from the condition $dx/dt = 0$) is given by

$$\bar{x} = \frac{w_f - w_u}{u/V} + x_0$$

being dependent only on x_0, the rates of formation and consumption of X, and the rate of flow, but not on the concentration of X in the vessel at the start of the continuous process.

The fact that the steady-state concentration is independent of the initial conditions can be illustrated, for example, by the series of kinetic curves for the accumulation of adipic acid in the autoxidation of cyclohexanone, obtained with different initial degrees of oxidation (Fig. 9).[15]

Autocatalytic reactions in which two stable steady states can occur depending on the initial conditions constitute an exception. This case has been analysed in the literature[14,34,41-43].

The possibility of more than one steady state appearing in such a system has been investigated in detail by Andreev[41] on the basis of an actual scheme for the oxidation of hydrocarbons in the presence of inhibitors which terminate the oxidation chains

$$RH \rightarrow RO_2^{\bullet} \qquad (w_0)$$
$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (k_2)$$
$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \qquad (k_3)$$
$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow \text{chain termination} \qquad (k_4)$$
$$RO_2^{\bullet} + \text{Inh} \rightarrow \text{chain termination} \qquad (k_i) .$$

The dependence of the steady-state concentration of radicals $\bar{n}$ on the initial concentration of inhibitor i_0 is found by solving the cubic equation

$$\bar{n}^3 - \frac{1}{k_6}\left(\frac{2k_2k_3[RH]}{(k_3+u/V)} - \frac{u}{V} - \frac{uk_5}{Vk_i}\right)\bar{n}^2 + \\ + \frac{u}{Vk_5k_i}\left(k_i \cdot i_0 - \frac{2k_2k_3[RH]}{(k_3+u/V)} + \frac{u}{V} - \frac{w_0k_i \cdot V}{u}\right)\bar{n} - \frac{u \cdot w_0}{Vk_ik_6} = 0 . \quad (11)$$

Equation (11) has three positive roots $\bar{n}_1$, $\bar{n}_2$, $\bar{n}_3$ (three steady states of the process) provided that

$$\frac{V}{u}\left[\frac{2k_2k_3[RH]}{(k_3+u/V)} - \frac{u}{V}\right] > \frac{k_5}{k_i}.$$

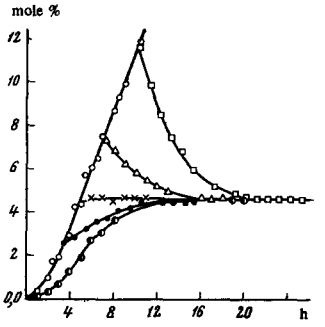


Figure 9. Kinetic curves for the accumulation of adipic acid during the continuous oxidation of cyclohexanone at 110°C with a rate of flow of 0.265 h^{-1}.

However, analysis shows that one of the solutions is unstable. The dependence of the steady-state concentration of the primary intermediate product, the hydroperoxide ROOH (the concentration of hydroperoxide is proportional to the concentration of radicals n), on the initial concentration of the inhibitor[42] is shown graphically[44] in Fig. 10. The section afb corresponds to the steady state $\bar{n}_1$, and the section cd determines $\bar{n}_3$. The state $\bar{n}_2$ (branch blc) is unsteady and is not realised.

Experimental data on the dependence of the steady-state concentration of a reaction product on the initial conditions have been obtained in an investigation of the inhibited oxidation of n-decane[42]. The steady-state hydroperoxide concentration is found to depend on the initial concentration of hydroperoxide in the system. Fig. 11 illustrates experimental results on the inhibited oxidation of pure n-decane and of n-decane containing 1.2 mole % of the hydroperoxide before the start of the reaction. The point a on this diagram indicates the steady-state hydroperoxide concentration in the absence of inhibitor, this being 0.8 mole % under the experimental conditions. If the pure hydrocarbon is being oxidised, the steady state of the system at high inhibitor concentrations is represented by the section c–d. At an inhibitor concentration corresponding to point c a sharp change occurs in the steady state of the system, in the direction indicated by the arrow. If the hydrocarbon contains a certain quantity of the hydroperoxide $[ROOH]_0 > a$ at the start of the reaction, the concentration of hydroperoxide in the steady state will vary along the section a–b with change in the inhibitor concentration right until the latter corresponds to point b. At this inhibitor concentration the steady state of the system changes in the direction indicated by the arrow. Thus it is seen that, with the same inhibitor concentration in the solution fed to the vessel and different initial hydroperoxide concentrations in the system ($[ROOH]_0$ = 1.2 mole % and 0), two markedly different steady states are attained. The broken section b–c defines the magnitude of the unstable steady state. In the oxidation of n-decane containing hydroperoxide from the start, breaks are observed close to the critical inhibitor concentration on the kinetic curve of the hydroperoxide (sections a–b on the curves in Fig. 12).[42]

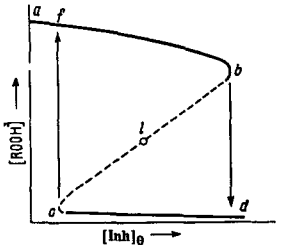


Figure 10. Dependence of steady-state concentration of hydroperoxide on initial concentration of inhibitor in a continuous process of oxidation (calculated results).

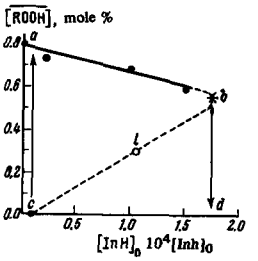


Figure 11. Dependence of steady-state concentration of hydroperoxide on concentration of 1-naphthol and initial hydroperoxide concentration in the system during the oxidation of n-decane with continuous supply of a solution of 1-naphthol in n-decane, at 135°C with rate of flow 1.45×10^{-4} s^{-1}.

With exothermic processes different steady states can be established according to the initial conditions even for simple types of reactions. The occurrence of two greatly differing régimes when a reaction is conducted under adiabatic conditions in a gradient-free reaction vessel was first established by Zel'dovich[43] for thermal ignition. It has been shown[34] that different steady states may be established, depending on the initial conditions, when a first-order exothermic reaction is conducted under non-isothermal conditions in a gradient-free vessel.

Thermal ignition phenomena with a sharp transition from a steady state to a non-stationary régime are inherent in exothermic processes even under static conditions. However, open systems are distinguished by sharper boundaries between ignition and a steady state. When exothermic processes are conducted in open systems, the possibility arises of determining the true concentration limit of ignition (this is impossible under static conditions because the mixture is consumed).

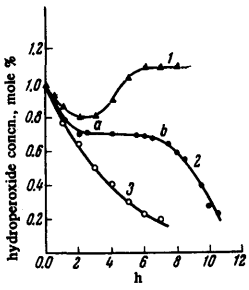


Figure 12. Kinetic curves for the accumulation of hydroperoxide in the oxidation of n-decane containing an initial hydroperoxide concentration of 1.0 mole % at 135°C with a rate of flow of 1.45×10^{-4} s^{-1}, and with different inhibitor concentrations (M) in the solution fed into the vessel: 1) 4.0×10^{-4}; 2) 4.1×10^{-4}; 3) 4.3×10^{-4}.

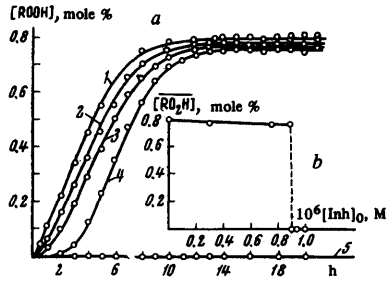


Figure 13. (a) Kinetic curves for the accumulation of hydroperoxide in the continuous oxidation of n-decane at 120°C, with rate of flow of 0.53 h^{-1}, in the presence of 1-naphthol (M): 1) 0; 2) 3×10^{-6}; 3) 7.5×10^{-6}; 4) 9.0×10^{-6}; 5) 9.05×10^{-6}. (b) Dependence of steady-state concentration of hydroperoxide on initial concentration of 1-naphthol.

A greater sharpness of critical transitions in open than in static systems has been observed also in an investigation of the inhibited oxidation of n-decane[45]. The inhibitors used were 1-naphthol and tri-(3,5-di-t-butyl-4-hydroxybenzyl)amine, under identical temperature conditions in open and static systems. When the process is conducted continuously a very sharp transition is observed from the autocatalytic reaction to the steady-state reaction at a critical inhibitor concentration[45] (Fig. 13). Under the same conditions in a closed system the induction period of the process increases linearly with increase in the inhibitor concentration, and limiting phenomena are not observed[42] (Fig. 14). The causes of the sharpness in the transitions in open systems have been analysed[42].

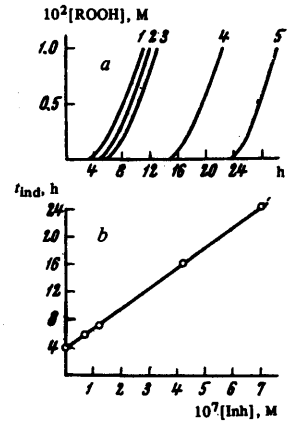


Figure 14. (a) Kinetic curves for the accumulation of hydroperoxide in the oxidation of n-decane under static conditions at 120°C with different initial concentrations (M) of inhibitor (1-naphthol): 1) 0; 2) 8×10^{-7}; 3) 1.2×10^{-6}; 4) 4.1×10^{-6}; 5) 7×10^{-6}. (b) Dependence of induction period on inhibitor concentration.

2. Dependence of Steady-state Concentration on Flow Rate

The variation in steady-state concentrations with change in the rate of supply of the starting materials has been discussed in the greatest detail in the literature. It has been shown for simple reactions (of the first, second, and third order) that increase in the rate of supply of starting materials (and of withdrawal of reaction products) diminishes the steady-state concentration of reaction products, while that of the starting materials increases monotonically[46].

As example let us examine the reaction $A \xrightarrow{k_1} C$, where conversion of A into the product is a first-order reaction. Then the variation in the concentrations of A and C will be described by the differential equations

$$\frac{d[A]}{dt} = -k_1[A] - \frac{u}{V}[A] + \frac{u}{V}[A]_0$$

$$\frac{d[C]}{dt} = k_1[A] - \frac{u}{V}[C],$$

where u is the bulk rate of supply of the substances, V is the volume of the system, $[A]_0$ is the concentration of A in the solution entering the vessel, and [A] and [C] are the instantaneous concentrations of A and C in the solution.

In the steady state $d[A]/dt = d[C]/dt = 0$, and the steady-state concentrations are

$$[\bar{A}] = \frac{(u/V)[A]_0}{(k_1 + u/V)} \quad (12)$$

$$[\bar{C}] = \frac{k_1[\bar{A}]}{u/V} = \frac{k_1[A]_0}{(k_1 + u/V)} \quad (13)$$

With increase in u/V the steady-state concentration of C will fall, while that of A will increase, since the factor $u/V(k_1 + u/V)$ increases with increase in u/V.

Analogous equations can be written for second- and third-order reactions[9,46].

The steady-state concentration of the intermediate product in a consecutive reaction will depend in more complicated fashion on the flow rate.

With increase in the rate of supply of the starting materials the steady-state concentration of the intermediate in the consecutive reaction A → B → C first increases and then falls. This extremal dependence on u/V is due to the fact that increasing this parameter produces an increase in the steady-state concentration of the initial substance A, which results in an increase in the concentration of B, while the more rapid removal of B from the system tends to diminish its steady-state concentration.

This can be illustrated by the interaction of the iron(III) ion with the thiosulphate ion[47]

$$2Fe^{3+} + 2S_2O_3^{2-} \rightarrow 2Fe^{2+} + S_4O_6^{2-}.$$

The reaction involves intermediate formation of an unstable complex between these two ions. Determination of the concentration of this complex has shown that its steady-state concentration passes through a maximum with increase in the rate of flow (Fig. 15).

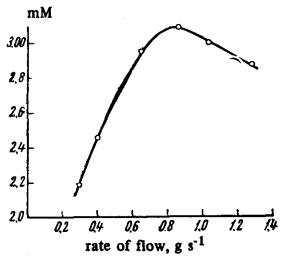


Figure 15. Dependence of steady-state concentration of intermediate complex in the reaction of Fe^{3+} with the thiosulphate ion on rate of supply of $S_2O_3^{2-}$ (rate of supply of Fe^{3+} constant at 0.388 g s^{-1}).

The rate of flow at which the maximum steady-state concentration of the intermediate is reached will depend on the rate constants of its formation and consumption[48]. In the simple consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, for example, the variation in the concentration of the intermediate substance B is given by the differential equation

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] - \frac{u}{V}[B].$$

The steady-state concentration of B is

$$[\bar{B}] = \frac{k_1 \frac{u}{V}[A]_0}{(k_1 + u/V)(k_2 + u/V)}. \qquad (14)$$

It is seen from Eqn. (14) that the steady-state concentration $[\bar{B}] \rightarrow 0$ as $u/V \rightarrow 0$ and as $u/V \rightarrow \infty$. Since $[\bar{B}]$ has some value different from zero within the range of variation of u/V from 0 to ∞, the steady-state concentration of B must pass through a maximum with increase in u/V. Differentiating $[\bar{B}]$ with respect to u/V, we obtain

$$\frac{d[\bar{B}]}{d(u/V)} = \frac{[A]_0 k_1 [k_1 k_2 - (u/V)^2]}{(k_1 + u/V)^2 (k_2 + u/V)^2}.$$

The dependence of $[\bar{B}]$ on u/V will pass through a maximum when $d[\bar{B}]/d(u/V) = 0$, i.e. at a rate of flow $u/V = \sqrt{k_1 k_2}$.

If more than one intermediate is formed in the system, the steady-state concentration of each product should pass through a maximum, and that of the first intermediate should be reached at higher rates of flow than that of the second intermediate[8]. Thus in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$ the maximum steady-state concentration of B is reached at a rate of flow u/V satisfying the condition $d[\bar{B}]/d(u/V) = 0$. For the steady-state concentration of the second intermediate C we have

$$\frac{d[C]}{dt} = k_2[B] - k_3[C] - u/V[C]; \quad [\bar{C}] = \frac{k_1[\bar{B}]}{k_3 + u/V}.$$

At the maximum in $[\bar{B}]$, when $d[\bar{B}]/d(u/V) = 0$, we find that

$$\frac{d[\bar{C}]}{d(u/V)} = -\frac{k_2[\bar{B}]}{(k_3 + u/V)^2} + \frac{k_2}{(k_3 + u/V)} \cdot \frac{d[\bar{B}]}{d(u/V)} < 0,$$

i.e. $[\bar{C}]$ is a diminishing function of u/V. This implies that the maximum value of C is reached at lower values of u/V than is $[\bar{B}]_{max}$.

The above rules for the variation in steady-state concentrations of final and intermediate products and of starting materials with rate of flow, derived for simple reactions, are maintained for more complicated processes.

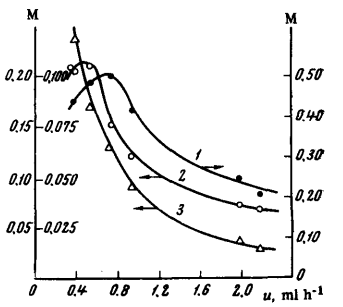


Figure 16. Dependence of steady-state concentrations of oxidation products on rate of supply of ethylbenzene at 118°C: 1) hydroperoxide (right-hand scale); 2) 1-phenylethanol (outer left-hand scale); 3) acetophenone (inner left-hand scale).

An example is the liquid-phase oxidation of ethylbenzene in the presence of azoisobutyronitrile as initiator[17]. The process goes by a chain mechanism with the following sequence of products

ethylbenzene → α-hydroperoxide → 1-phenylethanol → acetophenone

Thus two intermediate products—the hydroperoxide and the carbinol—and one final product—acetophenone—are formed in the system. Investigation of the oxidation of ethylbenzene in a gradient-free reaction vessel has shown that with increase in the flow rate the steady-state concentrations both of the hydroperoxide and of the carbinol pass through a maximum (Fig. 16). In complete agreement with what

has been stated above, the maximum steady-state concentration of the alcohol is reached at lower rates of flow than is that of the hydroperoxide. The steady-state concentration of the ketone falls monotonically with increase in u/V (Fig. 16).

Systems can also exist in which the above variation in steady-state concentration with rate of flow does not occur. Among them are processes involving the intermediate formation of complexes, e.g. by the scheme

$$\begin{aligned} A &\rightarrow B \quad (k_1) \\ B + C &\rightleftarrows D \quad (k_2, k_{-2}) \\ D &\rightarrow E \quad (k_3) \ . \end{aligned}$$

If equilibrium is established sufficiently rapidly and is not disturbed, either by conversion of D into E or by withdrawal of D from the system, i.e. provided that

$$k_3[D] \ll k_{-2}[D] \gg \frac{u}{V}[D]$$

the steady-state concentration of B will not pass through a maximum[49]. The steady-state concentration of A in such a system is

$$[\bar{A}] = \frac{(u/V)[A]_0}{(k_1 + u/V)}$$

while the rate of change in the concentration of B is described by the differential equation

$$\frac{d[B]}{dt} = k_1[A] - k_2[B][C] + k_{-2}[D] - \frac{u}{V}[B].$$

When thermodynamic equilibrium is maintained $k_2[B][C] = k_{-2}[D]$ and $d[B]/dt = k_1[A] - (u/V)[B]$. The steady-state concentration of the intermediate B

$$[\bar{B}] = \frac{k_1 V}{u}[A] = \frac{k_1[A]_0}{k_1 + u/V}$$

increases steadily with decrease in u/V, tending to $[A]_0$, and does not pass through a maximum.

The absence of a maximum steady-state concentration of an intermediate product has been shown for the oxidation of n-decane catalysed by cobalt stearate[21,49]. As already mentioned above (Section II, 2), breakdown of the hydroperoxide (intermediate product) in this process is preceded by formation of the complex ROOH.$CoSt_2$. Fig. 17 shows that the plot of [ROOH] against u/V does not reach a maximum down to relatively small rates of flow. The absence of a maximum is indicated also by the fact that in the uncatalysed oxidation of n-decane a maximum is reached at $u = 2.5$ ml h^{-1}. Yet it can be shown that increasing the rate of initiation by adding cobalt stearate should shift the maximum to higher rates of flow. Thus if ROOH is formed and consumed by a chain mechanism (with rate constants k_2 and k_3 respectively), the rate of flow at which a maximum steady-state concentration of the hydroperoxide is reached is

$$\frac{u}{V} = \sqrt{\frac{k_3 k_3}{k_6}}\sqrt{w_i}$$

(k_6 being the recombination constant of $RO_2^{\cdot}$ radicals), and increases with increase in the rate of initiation. Calculation of the scheme of catalysed oxidation (Section II, 2) on an M-20 electronic computer, with the equilibrium

$$ROOH + CoSt_2 \rightleftarrows ROOH \cdot CoSt_2$$

maintained, showed that the steady-state concentration of ROOH does not pass through a maximum up to 88% conversion of the starting material.

Variation in the rate of supply of the starting materials affects not only the steady-state concentrations of the individual reaction products but also the proportions of the products, since change in u/V influences the steady-state concentration of the final products to a far greater extent than that of the intermediates. This effect is especially clearly developed in the oxidation of cyclohexanone by oxygen at 110°C.[15] With change in the rate of supply of cyclohexanone from 0.079 to 1.175 h^{-1} the steady-state concentration of the hydroperoxide changes from 0.298 to 0.242 mole %, i.e. by a factor of 1.2, whereas the steady-state concentration of adipic acid changes by a factor of 12.

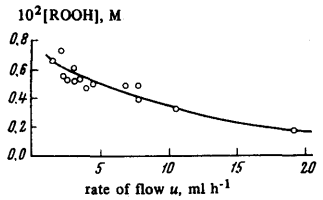


Figure 17. Dependence of steady-state hydroperoxide concentration on rate of flow in the oxidation of n-decane catalysed by cobalt stearate ($[CoSt_2]_0$ = 0.006 M) in a reaction vessel of ideal mixing at 130°C.

Furthermore, when cyclohexanone is oxidised in a gradient-free reaction vessel, the extent of oxidation of adipic acid to carbon dioxide is considerably diminished. If with 4.5 mole % of adipic acid the rate of evolution of carbon dioxide per mole of adipic acid is 0.124 mole h^{-1} under static conditions, in an open system it is only 0.032 mole h^{-1}.

In general in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$ increase in the rate of supply of the starting materials will enrich the mixture in the intermediate products. Thus the concentration of C in the steady state is given by

$$k_2[\bar{B}] - (k_3 + u/V)[\bar{C}] = 0, \text{ whence } \frac{[\bar{B}]}{[\bar{C}]} = \frac{(k_3 + u/V)}{k_2}.$$

With increase in u/V the ratio $[\bar{B}]/[\bar{C}]$ increases: i.e. the relative content of B in the mixture of reaction products is increased.

This conclusion may not apply to more complicated reactions, such as the oxidation of organic compounds[10]. Analysis of a process of oxidation involving chain branching by the reaction $ROOH \xrightarrow{k_3} HO^{\cdot} + RO^{\cdot}$ and quadratic recombination of radicals ($RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_6}$ products) shows that the ratio of the steady-state concentrations of the hydroperoxide (ROOH) and a product C, the latter formed from the hydroperoxide by a molecular mechanism (constant k) and consumed by a chain mechanism§ (constant k_4), is given by

$$\eta = \frac{[\overline{ROOH}]}{[\bar{C}]} = \frac{k_3 \cdot k_3 k_4 [RH]}{k k_6 (k + u/V)} + \frac{u/V}{k}$$

§ If the reaction product is not used up or is consumed by a molecular mechanism, this scheme yields a result identical with that obtained from consideration of a simple consecutive reaction.

in which k_2 is the rate constant of chain propagation $RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$. It is seen from this expression that the ratio of the steady-state concentrations increases at small rates of flow, but with further increase in u/V it falls. The maximum value of η is attained at the rate of flow

$$u/V = \sqrt{\frac{k_2 k_3 k_4 [RH]}{k_6}} - k.$$

Thus with consecutive chain reactions variation in the flow rate over a certain range may result in enrichment of the mixture with the first intermediate, and over another range enrichment with the second intermediate. The concentration ratio of intermediate and final products increases steadily, as with simple consecutive reactions[10].

With variation in the rate of supply of ethylbenzene the ratio of the steady-state concentrations of the hydroperoxide and 1-phenylethanol formed by its oxidation passes through a maximum (Fig. 18).[17] At the same time the ratio of the steady-state concentrations of the hydroperoxide and of acetophenone (AcPh) increases monotonically, as can be seen from the following data

u, ml h^{-1}	0.40	0.55	0.75	0.95	2.0	2.2
$[\overline{ROOH}]/[\overline{AcPh}]$	5.2	5.7	8.1	9.3	15	15.7

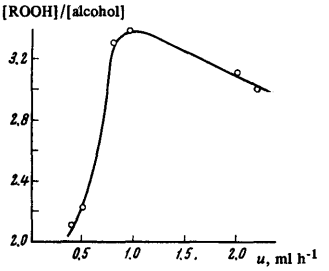


Figure 18. Dependence of ratio of steady-state concentrations of hydroperoxide [ROOH] and 1-phenylethanol on the volume flow rate of ethylbenzene to a reaction vessel with ideal mixing at 118°C.

In concluding this Section it is appropriate to mention that the maximum steady-state concentration attainable in an open system is always lower than the maximum concentration of a product under static conditions with the same process conditions. Thus in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ the steady-state concentration of the final product C

$$[\overline{C}] = \frac{[A_0] k_1 k_2}{(k_1 + u/V)(k_2 + u/V)}$$

is always lower than the maximum possible concentration $[C] = [A]_0$ under static conditions, and tends to it as the rate of flow diminishes. The maximum possible steady-state concentration of the intermediate product B, attainable at a rate of flow $u/V = \sqrt{k_1 k_2}$, is

$$[\overline{B}]_{max} = \frac{[A]_0 \cdot k_1}{(\sqrt{k_1} + \sqrt{k_2})^2}.$$

Yet for the maximum concentration of this product under static conditions[11] we have

$$[B]_{max} = [A]_0 \left(\frac{k_2}{k_1}\right)^{k_1/(k_1 - k_2)}.$$

Writing $k_2/k_1 = \kappa$, we find that the ratio of the maximum concentration of B under static conditions to its maximum concentration in an open system is

$$y = \frac{[\overline{B}]_{max}}{[B]_{max}} = \frac{\kappa^{\frac{\kappa}{1-\kappa}}}{(\sqrt{\kappa} + 1)^2}.$$

Hence it follows[10] that at all values of κ the function $y = y(\kappa)$ is less than unity: i.e. $[B]_{max}$ always exceeds $[\overline{B}]_{max}$.

The calculations given here are valid, of course, only for a simple consecutive reaction. The influence of further complication of the system on the ratio of the maximum concentrations in open and closed systems requires special examination.

V. DEPENDENCE OF REACTION VELOCITY ON FLOW RATE IN VESSELS HAVING IDEAL MIXING

The rate of change in the concentration of any substance in an open system, as already mentioned above, is given by

$$\frac{d[C]}{dt} = w_f + w_u - \frac{u}{V}[C]$$

In the steady state $(u/V)[C] = w_f - w_u$. Thus the product of the rate of supply of the starting materials by the steady-state concentration of a given substance gives the rate of accumulation of this substance in the reaction. In an open system, as under static conditions, the reaction velocity changes with the extent of the process.

For reactions of the first, second, and third order the reaction velocity (the rate of consumption of the starting material) is a maximum at the maximum concentration of the starting materials[46]. In this case, therefore, the maximum reaction velocity is reached with the maximum possible rates of supply of the starting materials. In practice, however, such rates are used very rarely, owing to the difficulty of isolating the reaction products from dilute solutions.

Let us examine the variation with the rate of flow in the rates of accumulation of intermediate and final products in the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$.[8] The steady-state concentration of the intermediate product B is (see Section IV, 2)

$$[\overline{B}] = \frac{[A]_0 k_1 \cdot u/V}{(k_1 + u/V)(k_2 + u/V)}.$$

Hence its rate of accumulation

$$\frac{u}{V}[\overline{B}] = \frac{[A]_0 k_1 (u/V)^2}{(k_1 + u/V)(k_2 + u/V)}$$

increases monotonically with increase in the rate of supply of the starting materials, as in the case of the reaction $A \rightarrow B$, where B undergoes no further change.

For the final product C we have correspondingly

$$\frac{u}{V}[\overline{C}] = \frac{[A]_0 k_1 k_2 u/V}{(k_1 + u/V)(k_2 + u/V)}; \quad \frac{d(u/V\,[C])}{d(u/V)} = \frac{[A]_0 k_1 k_2 [k_1 k_2 - (u/V)^2]}{(k_1 + u/V)^2 (k_2 + u/V)^2}$$

It is seen that, when $u/V > \sqrt{k_1 k_2}$, the derivative

$$\frac{d\left(\frac{u}{V}[\bar{C}]\right)}{d(u/V)} < 0$$

and the rate of accumulation of the final product falls with increase in u/V. When $u/V < \sqrt{k_1 k_2}$, we have

$$\frac{d(u/V\,[\bar{C}])}{d(u/V)} > 0,$$

i.e. the quantity $[\bar{C}]u/V$ increases with increasing rate of supply of the starting materials. Thus the dependence of rate of accumulation of the product C on u/V passes through a maximum at $u/V = \sqrt{k_1 k_2}$. This same rate u/V corresponds to the maximum steady-state concentration of the intermediate product (Section IV, 2).

If in a consecutive reaction A → B → C the product B is formed autocatalytically from its precursor, not only the rate of accumulation of C but also that of B and even the rate of consumption of A should pass through a maximum with increase in the rate of flow[8]. An extremal dependence of the overall rate of the process and the rate of accumulation of each product on the rate of supply of the initial substances is observed in an open system whenever the kinetic curve for accumulation of the given product under static conditions is S-shaped.

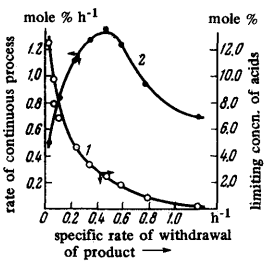


Figure 19. Dependence, on specific rate of supply of cyclohexanone during its continuous oxidation at 110°C, of: 1) steady-state concentration of adipic acid; 2) rate of accumulation of adipic acid.

In the oxidation of cyclohexanone in an open system the rate of accumulation of adipic acid first increases with increase in u/V, passes through a maximum, and then falls[15] (**Fig. 19**). Analogous extremal variations in the rate of consumption of hydrocarbon and of accumulation of each of the reaction products with increase in u/V have been observed also in the oxidation of n-decane at 140°C (Fig. 20).[8] It is seen from Fig. 20 that the rates of accumulation of all the products of the reaction pass through a maximum, including the rate of accumulation of the first intermediate product, the hydroperoxide. The maxima in the rates of accumulation of all the products with variation in the flow rate are displaced relative to each other, being reached at different flow rates.

With the simple consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$ as example it has been shown[10] that the maximum rates of accumulation of the individual reaction products should be observed at different values of u/V. For the accumulation of C and D we can write the differential equations

$$\frac{d[C]}{dt} = k_2[B] - (k_3 + u/V)[C] = 0; \quad \frac{d[D]}{dt} = k_3[C] - \frac{u}{V}[D] = 0.$$

Hence the rates of accumulation of these products are

$$\frac{u}{V}[\bar{C}] = \frac{k_2[\bar{B}]\,u/V}{(k_3 + u/V)}; \quad \frac{u}{V}[\bar{D}] = k_3[\bar{C}] = \frac{k_2 k_3 [\bar{B}]}{(k_3 + u/V)}$$

The maximum rate of accumulation of D is reached when

$$\frac{d}{d(u/V)}\left[\frac{[\bar{B}]}{(k_3 + u/V)}\right] = 0;$$

and the maximum rate of accumulation of C when

$$\frac{d\left[\frac{u}{V}[C]\right]}{d(u/V)} = k_2 \frac{u}{V} \frac{d}{d(u/V)}\left[\frac{[\bar{B}]}{(k_3 + u/V)}\right] + \frac{k_2[\bar{B}]}{(k_3 + u/V)} = 0.$$

At the point $d(u[\bar{D}]/V)/d(u/V) = 0$ we have $d(u[\bar{C}]/V)/d(u/V) > 0$: i.e. the maximum rate of accumulation of C is reached at higher values of u/V than is that of D. If one of the stages in the sequence or all of the stages in this process are autocatalytic, the maximum rates of accumulation of individual products are also observed at different rates of flow.

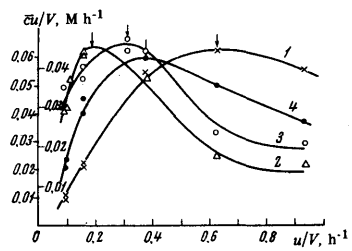


Figure 20. Dependence, on rate of supply of n-decane during its oxidation in reaction vessel of ideal mixing at 140°C, of rates of accumulation of: 1) hydroperoxides (outer scale); 2) acids (outer scale); 3) ketones (inner scale); 4) alcohols (inner scale).

As already remarked above, the maximum rate of accumulation of any final product of a simple consecutive reac- A → B → C is reached at the same rate of supply of the starting materials as is the maximum steady-state concentration of the intermediate which is the immediate precursor of the given final product (see above), independently of whether B can be consumed only by conversion into C or in more than one way. This property of an open system has yielded a possible method for determining the routes by which the final reaction products are formed.

The method consists in comparing the maximum rates of accumulation of the final products and the steady-state concentrations of the intermediates with variation in the flow rate. If these maxima are reached at the same flow rate, the intermediate can be regarded as the direct precursor of the given final product[8].

However, this method of determining the paths by which the final products are formed is not general, and requires careful analysis of the mechanism and the conditions under

which the process is conducted. Thus in the autocatalytic consecutive reaction A → B → C → D, where the reaction product B accelerates consumption of C, the maximum rate of accumulation of D and the maximum steady-state concentration of C should be reached at different values of u/V. However, some modification of the method enables the paths by which D is formed to be determined even in this case[10].

Analysis of the scheme for a chaim oxidation in the liquid phase, where the product D is formed by a chain mechanism involving free peroxy-radicals $RO_2^{\cdot}$ formed by the breakdown of B (with a rate constant k_2'), shows that the rate of accumulation of D in this case is $u[\bar{D}]/V = k_3[\bar{C}][RO_2^{\cdot}]$, or $u[\bar{D}]/V = k_3(k_2'[\bar{B}][\bar{C}]/k_6)^{1/2}$, since with quadratic recombination of radicals (rate constant k_6) we have $[RO_2^{\cdot}] = (k_2'[\bar{B}]/k_6)^{1/2}$.

Since the amount of B is affected by change in the flow rate, the maxima in the relations $u[\bar{D}]/V = f_1(u/V)$ and $u[\bar{C}]/V = f_2(u/V)$ will not coincide. However, if a substance which will ensure a sufficiently rapid rate of formation of radicals $RO_2^{\cdot}$ is added to the system together with the starting materials, so that $w_i > k_2'[\bar{B}]$, we have

$$u/V\,[\bar{D}] = k_3[\bar{C}][RO_2^{\cdot}] = \frac{k_3[\bar{C}]}{\sqrt{k_6}}\sqrt{w_i}$$

By varying the initiator concentration so that w_i remains constant with variation in the flow rate, these maxima can be made to coincide.

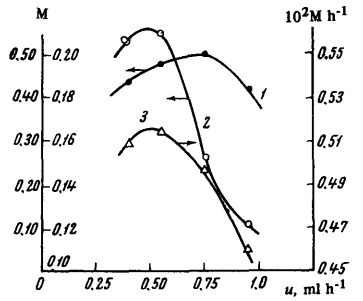
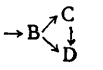


Figure 21. Dependence, on rate of supply of ethylbenzene at 118°C, of: 1) steady-state concentration of hydroperoxide; 2) steady-state concentration of 1-phenylethanol; 3) rate of accumulation of acetophenone.

The method has been tested for the oxidation of ethylbenzene[17]. (Preliminary experiments had shown that acetophenone was formed directly from 1-phenylethanol, not by decomposition of the hydroperoxide—see below.) Fig. 21 illustrates the dependence of the rates of accumulation of acetophenone and of the steady-state concentrations of ethylbenzene hydroperoxide and 1-phenylethanol on the rate of supply of ethylbenzene. The rate of initiation of chains was maintained constant to ±4% while u/V was varied from 0.096 to 0.041 h^{-1}. It is seen from Fig. 21 that the maximum rate of accumulation of acetophenone is reached at the same value of u/V as is the maximum steady-state concentration of 1-phenylethanol.

When the final product in a complicated consecutive-parallel reaction is formed by two or more parallel routes, it is also possible to establish these paths. Thus it has been shown[10], for example, that in the consecutive-parallel reaction



the maximum steady-state concentration of B is reached at the same value of u/V as is the total rate of accumulation of the products C and D.

VI. USE OF REACTIONS IN VESSELS HAVING IDEAL MIXING AS METHOD OF INVESTIGATING THE MECHANISM OF CHEMICAL REACTIONS

Study of the kinetics of reactions in vessels with ideal mixing enables the paths by which the final products are formed to be assessed from the dependence of the steady-state concentrations of the intermediate substances and the rates of accumulation of the final products on the rate of flow. However, this is not the only possibility for studying reaction mechanisms and rates of formation of products provided by open systems.

One of the greatest advantages of open systems is that the use of gradient-free reaction vessels makes it possible to study a reaction under perfectly constant experimental conditions, for variation in the conditions during an experiment makes it difficult to interpret the results. The influence of such factors as the pH of the medium, the dielectric constant, etc. is far more easily established when the reaction is conducted in an open system, where constant conditions can be maintained as long as desired.

Such systems present a considerable advantage also for the study of rapid chemical reactions. This method has been used, for example, to study the rapid interaction of iron(II) ions with sodium thiosulphate[47]. The reaction involves the intermediate formation of a violet complex. Under static conditions the coloration disappears extremely rapidly, and it is practically impossible to obtain the spectrum of this compound. Conducting the reaction in an open system with solutions of sodium thiosulphate and of an iron salt fed separately to the vessel enabled the spectrum of the intermediate complex to be obtained. At sufficiently high rates an intense violet coloration was established, which was stable with time and enabled the absorption spectrum of the complex to be recorded. The lifetime of the complex was found to be 10 s.

The attainment of steady-state concentrations when chemical reactions are conducted in gradient-free reaction vessels simplifies mathematical analysis of the set of kinetic equations describing the process. This in turn considerably facilitates the task of determining the rate constants for reactions of differing order from known concentrations of the reaction components.

1. Determination of Rate Constants for Simple Types of Reactions

The rate constants of first-order reactions in open systems can be determined quite simply[50] both from the steady-state concentration of starting material or final product (see Eqns. 12 and 13) and from the time required to reach half the steady-state concentration (Eqn. 3a). These formulae do not take into account a possible change in volume during the reaction. Yet most first-order reactions in the gas phase involve a change in volume. Use

of the formulae (13) and (12) then becomes impossible because of the inequality in the rates of withdrawal of products and supply of starting materials, so that the formula

$$k_1 = \frac{(u/V)[A]_0 - (u/V)_1[\bar{A}]}{[\bar{A}]}$$

where u/V is the rate of supply and $(u/V)_1$ the rate of withdrawal of the starting material A from the system, must be applied[51].

It is thus sufficient to know merely the speed of the gas on entering and on leaving the vessel in order to determine the rates of the process. Nevertheless, a change in volume during the process greatly increases the difficulty of studying reactions in a laminar flow system, since it is then necessary to know the law governing the change in volume throughout the length of the vessel.

As example of the determination of a first-order rate constant we can cite the gas-phase decomposition of chlorocyclohexane (A), which is accompanied by the evolution of elementary chlorine[52]. Progress of the reaction was followed from the change in concentration of chlorine. Since the process involves a change in volume, the rate of withdrawal of chlorine from the system is not equal to the rate of supply of chlorocyclohexane. The rate of change in the chlorine concentration can be written

$$\frac{d[Cl_2]}{dt} = k_1[A] - \frac{u_{Cl_2}}{V}[Cl_2]$$

where u_{Cl_2} is the space velocity of removal of chlorine from the system. After a steady-state chlorine concentration has been established, when $d[Cl_2]/dt = 0$, the constant k_1 is determined by means of the formula

$$k_1 = \frac{u_{Cl_2}}{V}\frac{[\bar{Cl}_2]}{[\bar{A}]}.$$

The value obtained for the decomposition rate constant of chlorocyclohexane was identical with that determined previously under static conditions, which indicates that reaction rate constants can be determined by this method.

A similar study has been made of the pyrolysis of ethyl acetate, which is also a first-order reaction accompanied by a change in volume[53]. The rate constant was determined over the temperature range 376–531 °C, and it was found that the activation energy varied with temperature.

The possibility of determining the rate constants of bimolecular reactions has been examined in detail for the reaction $A + B \xrightarrow{k} C$. In this case k can be determined by measuring the concentration of at least one of the substances present in the system (e.g. C), provided that the initial concentrations a_0 and b_0 of A and B in the mixture entering the vessel are known, together with the rate of supply of A and B to the system[50]. Thus if A and B enter the system with different space velocities u_A and u_B, while the reaction product is removed from the system at the rate $u = u_A + u_B$, the constant is determined by means of the formula

$$c = \frac{(V/u)\ k\ (u_A \cdot a_0 - u \cdot c)\ (u_B \cdot b_0 - u \cdot c)}{u^2}.$$

The rate constant of a bimolecular reaction in a gradient-free reaction vessel was first measured by Bodenstein[1], as already mentioned.

Use of a reaction vessel with ideal mixing facilitates the task of determining the rate constants not only of simple but also of complicated, multistage reactions, among which are consecutive, parallel, and consecutive–parallel reactions.

The individual rate constants of each process can be determined for a series of parallel reactions. In one of the simplest cases, e.g. when several parallel reactions

$$\begin{aligned} A_1 + B &\rightarrow C_1 \quad (k_1)\\ A_2 + B &\rightarrow C_2 \quad (k_2)\\ &\cdots\\ A_n + B &\rightarrow C_n \quad (k_n) \end{aligned}$$

are occurring in a system, each of the constants can be determined by conducting the process with various rates of supply of the starting materials, only the steady-state concentration of these substances being measured. In fact, the rate of change in the concentration of B is

$$\frac{d[B]}{dt} = -k_1[A_1][B] - k_2[A_2][B] - \ldots - k_n[A_n][B] - \frac{u}{V}[B] + \frac{u}{V}[B]_0. \quad (15)$$

When $d[B]/dt = 0$, this equation is converted into an algebraic equation, in which all the k_i can be determined provided that there are n such equations. If the parallel reactions take place in the gas phase and are accompanied by change in volume, the formulae for calculating the individual constants are somewhat complicated[51].

The rate constants of parallel reactions have been determined for the gas-phase decomposition of isopropyl and s-butyl chloroformates, which is accompanied by change in volume[52,53]. When the gaseous compounds are heated to high temperatures, they may undergo either substitution or decomposition with formation of alkenes; in the case of the s-butyl ester, two stereoisomeric compounds—*cis*- and *trans*-but-2-ene—can be formed. Conducting these processes in an open system has enabled the rate constants of each of the parallel stages to be determined at various temperatures.

In the case of a simple consecutive reaction of the type $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ with the same rate of supply of the starting materials, both constants can be determined from the steady-state concentrations of the initial and intermediate substances (A and B) by means of the equations¶

$$-k_1[\bar{A}] - \frac{u}{V}[\bar{A}] + \frac{u}{V}[A]_0 = 0 \quad (16)$$

$$k_1[\bar{A}] - k_2[\bar{B}] - \frac{u}{V}[\bar{B}] = 0. \quad (17)$$

If the concentration of the intermediate cannot be measured, the constants k_1 and k_2 can be determined from the steady-state concentrations of the final reaction product (C) with various rates of supply of the starting materials, by means of the formula

$$[\bar{C}] = \frac{k_1 k_2 [A]_0}{(k_1 + u/V)(k_2 + u/V)}$$

or

$$\frac{1}{u/V}\left\{\frac{1}{[\bar{C}]} - \frac{1}{[A]_0}\right\} = \frac{1}{k_1 k_2}(k_1 + k_2) + \frac{1}{k_1 k_2} \cdot \frac{u}{V}.$$

In the latter case, by plotting

$$\frac{1}{u/V}\left(\frac{1}{[\bar{C}]} - \frac{1}{[A]_0}\right)$$

against u/V, we can determine k_1 and k_2 separately.

Determination of the rate constants for all stages in a process is possible also when a common component takes

¶ Use of an analogous method under static conditions necessitates the graphical differentiation of the kinetic curves for the consumption of A and the accumulation of B, which diminishes the accuracy of the constants obtained.

part in every stage in a consecutive bimolecular reaction[54]. The possibility of determining rate constants for consecutive bimolecular reactions has been examined in detail for chlorinations represented by the scheme

$$A + B \xrightarrow{k_1} A_1$$
$$A_1 + B \xrightarrow{k_2} A_2 \text{ etc.}$$

In this case the constant k_1 can be determined from the formula

$$k_1 = \frac{u}{V \cdot a \cdot x}(1-a) \qquad (18)$$

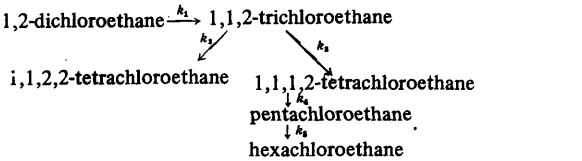
where a is the steady-state mole fraction of A in the reaction vessel, while x is the number of moles of chlorine which have reacted per mole of the initial substance A consumed. The value of x is given by the sum of the mole fractions of all the chlorinated reaction products multiplied by the appropriate coefficients:

$$x = a_1 + 2a_2 + 3a_3 + \ldots + na_n$$

The constant k_2 can be determined if the steady-state mole fractions of A and A_1 are known:

$$k_2 = \frac{u}{V} \cdot \frac{1}{a_1 x}(1-a_1-a_2). \qquad (19)$$

The above formulae (18) and (19) have been used to determine the rate constants for the chlorination of 1,2-dichloroethane at 100°C, which is represented by the scheme



The constants k_1, k_2, and k_3 were determined in the chlorination of 1,2-dichloroethane, and it was shown that 1,1,2,2-tetrachloroethane does not undergo further chlorination. The constants k_4 and k_5 were measured in the chlorination of 1,1,2-trichloroethane[55] and of 1,1,1,2-tetrachloroethane[56] under analogous conditions.

Conducting a process in open systems enables not only the rate constants but also the order of the reaction to be determined. If a reaction of the nth order with respect to some component, e.g. $nA \rightarrow B$, is conducted in an open system with different rates of supply $(u/V)_1$ and $(u/V)_2$ of the starting materials, the steady-state concentrations $[\bar{A}]_1$ and $[\bar{A}]_2$ are given by

$$k[\bar{A}]_1^n = \left(\frac{u}{V}\right)_1 ([A]_0 - [\bar{A}]_1) \qquad (20)$$

$$k[A]_2^n = \left(\frac{u}{V}\right)_2 ([A]_0 - [\bar{A}]_2) \qquad (21)$$

Dividing Eqn. (20) by (21) term by term and taking logarithms, we obtain

$$n \lg \frac{[\bar{A}]_1}{[\bar{A}]_2} = \lg \left\{ \frac{u_1}{u_2} \cdot \frac{([A]_0 - [\bar{A}]_1)}{([A]_0 - [\bar{A}]_2)} \right\},$$

the slope of the plot of $\lg([\bar{A}]_1/[\bar{A}]_2)$ against the right-hand side of this equation giving the order n of the reaction.

Determination of the order of a reaction is a far more laborious task in open systems than under static conditions, since it requires many experiments to be made, whereas under static conditions a kinetic curve with a practically unlimited number of points is obtained in one experiment. Nevertheless, in several complicated processes the order with respect to some component is better determined in open systems. Among such reactions are all those processes in which change in the composition of the product during the reaction changes the apparent order of the reaction.

Thus, for example, the order of the polymerisation of styrene in the presence of an initiator—benzoyl peroxide—has not been accurately established. From some results it has been assumed that the reaction is of the first order with respect to the monomer, whereas other results indicate an order of 1.5. Study of this process in open systems has shown[12] that the apparent order of the reaction with respect to the monomer varies from 1.18 to 1.36 depending on the composition of the reactant mixture.

A property of open systems which is among the most valuable for the study of reaction mechanisms is the possibility of investigating the reaction over a wider temperature range—both downwards and upwards—than under static conditions.

When reactions are studied in open systems, it becomes possible to conduct processes at very small degrees of conversion, which cannot be used under static conditions because of analytical difficulties. The practically unlimited volumes of gases or liquids leaving the reaction vessel in open systems make it possible to accumulate analytically detectable amounts of products even at low degrees of conversion. As a consequence, the temperature of the reaction can be considerably lowered in comparison with static conditions.

At the same time the continuous supply of starting materials to the system prevents them from being completely burned out, so that reactions in open systems can be conducted at considerably higher temperatures than under static conditions. Thus in an investigation[52] of the thermal decomposition of chlorocyclohexane in the gas phase in a flow-type reaction vessel with stirring, it proved possible to raise the temperature from 385°C (the maximum temperature at which the decomposition of this substance had been studied under static conditions) to 476°C, i.e. by almost 100 deg. Study of the decomposition of ethyl acetate in open systems over a wide temperature range enabled a change in mechanism of pyrolysis with rise in temperature to be detected[53]: at high temperatures (above 500°C) the activation energy of pyrolysis is 44 kcal mole^{-1}, but when the temperature is lowered to 376–414°C the activation energy falls to 41 kcal mole^{-1}.

The possibility of determining rate constants for simple types of reactions, as well as for parallel and consecutive reactions, is undoubtedly a merit of open systems. In most cases, however, especially for simple types of reactions, these constants can easily be determined also under static conditions.

The advantage of "open" systems over all other methods of conducting a process is shown most clearly when it is necessary to study complicated reactions. Variation in conditions during the process (e.g. change in the ionic strength of the solution, the dielectric constant, the pH, etc.) makes the determination of rate constants under static conditions extremely inaccurate, and interpretation of the results difficult. To maintain the ionic strength, pH, etc. constant under static conditions special methods are used (e.g. buffer solutions or continuous titration of the solutions during the process, which changes the volume of the system and thereby introduces additional difficulties).

Open systems enable a process to be conducted under conditions which remain unchanged for a long time, so that the reaction velocity can be measured accurately with the composition of the reaction mixture rigidly fixed. An

example is provided by the bromination of acetone under conditions of ideal mixing[57]. The rate constant of this process, determined from the scheme for a simple consecutive reaction, varies considerably with the extent of reaction, so that it was concluded that this reaction is more complicated than the scheme adopted in the literature.

2. Determination of Rates of Reactions involving Reactive Intermediates

The method described above for determining the rate constants of individual stages in parallel and consecutive reactions cannot always be used to determine the rates of chain reactions involving active intermediate species, whose concentration is often impossible to measure.

The kinetics of the accumulation of an intermediate B in consecutive chain reactions, e.g. $A \xrightarrow{RO_2^\cdot} B \xrightarrow{RO_2^\cdot} C$, in an open system is described by the equation

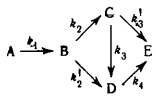
$$\frac{d[B]}{dt} = k_1[RO_2^\cdot][A] - k_2[RO_2^\cdot][B] - \left(\frac{u}{V}\right)[B] = 0. \qquad (22)$$

If the steady-state concentration of the initial substance A is known, Eqn. (22) can be used, together with the equation

$$\frac{d[A]}{dt} = -k_1[RO_2^\cdot][A] - \frac{u}{V}([A] - [A]_0) = 0 \qquad (23)$$

for the consumption of A, to determine the products $k_1[RO_2^\cdot]$ and $k_2[RO_2^\cdot]$, and hence the separate rates of formation and consumption of B for a given rate of supply of the substances.

In general, if the number of unknown rate constants exceeds the number of component concentrations which can be measured, it is impossible to determine the rates of formation and consumption of a substance from an experiment conducted at a single rate of flow. For example, the sequence of reactions



in the steady state can be described by a set of five equations with six unknown constants, and it becomes possible to determine all the constants only by conducting the reaction with several different velocities. In several cases, however, change in the rate of flow has a complicated effect on the concentration of free radicals, and separate determination of the rates of formation and of consumption of intermediates becomes impossible.

The rates of formation and consumption of products in chain reactions are now being very successfully measured by a kinetic method of labelled atoms, in which small additions of intermediates labelled with a radioactive isotope are introduced into the system[58]. However, the method is quite laborious, and involves isolation of the given intermediate from a complicated mixture of reaction products, which is often a quite difficult task. Use of the labelled atoms method in an open system[59] makes this problem slightly easier.

A new method has recently been suggested for determining the rates of formation of intermediates[60]. It consists in conducting the reaction in an open system until a steady state is established. From then a certain quantity of the intermediate, whose rates of formation and consumption are to be measured, is added to the reaction vessel together with the starting material. The bulk rate of supply of the substance to the vessel should not be varied. In this case the steady-state concentrations of the initial substance and of the branched product (and hence also the steady-state concentration of free radicals) remain unchanged, since the rate of supply of the starting materials is constant. The difference in the steady-state concentrations of the intermediate established in the two cases enables its rates of formation and consumption in the system to be determined†.

In the consecutive reaction $A \xrightarrow{RO_2^\cdot} B \xrightarrow{RO_2^\cdot} C$ the steady-state concentration of B when only the initial substance A is fed to the system is given by the equation

$$k_1[RO_2^\cdot][\bar{A}] - k_2[RO_2^\cdot][\bar{B}] - \frac{u}{V}[\bar{B}] = 0 \qquad (24)$$

but when solutions containing additions of B at concentration $[B]_0$ are supplied we have

$$k_1[RO_2^\cdot][\bar{A}] - k_2[RO_2^\cdot][\bar{B}]_1 - \frac{u}{V}[\bar{B}]_1 + \frac{u}{V}[B]_0 = 0. \qquad (25)$$

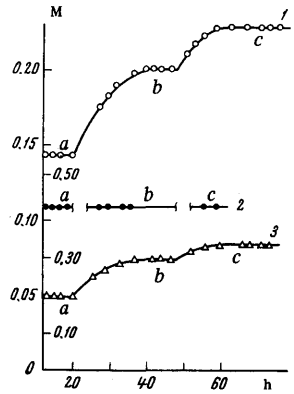


Figure 22. Oxidation of ethylbenzene in reaction vessel of ideal mixing at 118°C, with rate of flow 0.102 h^{-1}, during supply of ethylbenzene (sections a) and of 0.106 M and 0.17 M solutions of 1-phenylethanol in ethylbenzene (sections b and c). Kinetic curves for the accumulation of: 1) alcohols (outer scale); 2) hydroperoxides (inner scale); 3) ketones (outer scale).

As mentioned above, the steady-state concentrations of A and $RO_2^\cdot$ are not affected by supplying to the system a solution containing B. Solution of Eqns. (24) and (25) gives

$$\left(1 + \frac{k[RO_2^\cdot]V}{u}\right) = \frac{[B]_0}{[\bar{B}]_1 - [\bar{B}]} \qquad (26)$$

For a first-order reaction $[\bar{B}]_1 - [B]$ can be plotted against $[B]_0$, the slope giving $k_2[RO_2^\cdot]$, from which $k_1[RO_2^\cdot]$ can be calculated, as well as the ratio of the rate constants for formation and consumption of B. If B is consumed by an nth-order reaction, Eqn. (26) becomes

$$\frac{k_2[RO_2^\cdot]V}{u} = \frac{[B]_0 + [\bar{B}]^n - [\bar{B}]_1^n}{[\bar{B}]_1 - [\bar{B}]} \qquad (27)$$

† This method cannot be used if addition of the intermediate has a substantial effect on the rate of chain branching.

Use of this method to study the autoxidation of n-decane and ethylbenzene has yielded the ratios of the rate constants for interaction of $RO_2^{\cdot}$ radicals with the alcohol, the hydroperoxides, and the hydrocarbon[60-62]. For example, the rate of formation of 1-phenylethanol in the oxidation of ethylbenzene has been determined from experiments in which 0.106 M and 0.17 M solutions of the alcohol in ethylbenzene were supplied to the vessel. Fig. 22 shows that the steady-state concentrations of the alcohol (*1*) and of acetophenone (*3*) increase. The constancy of the hydroperoxide concentration (*2*) indicates that the concentration of radicals remains unchanged for all additions of the alcohol. The steady-state concentrations of 1-phenylethanol (B) obtained are plotted in Fig. 23 as $[\bar{B}]_1 - [\bar{B}]$ against $[B]_0$. From the slope of the straight line obtained it was calculated that $k_2[RO_2^{\cdot}] = 0.15\ min^{-1}$. The same method has been used to measure the rates of formation and consumption of products of the oxidation of n-decane catalysed by cobalt stearate. In this process the greater part of the alcohols, ketones, and acids were shown to be formed directly from the $RO_2^{\cdot}$ radicals[63], not by decomposition of a hydroperoxide (as occurs in the absence of a catalyst[44]).

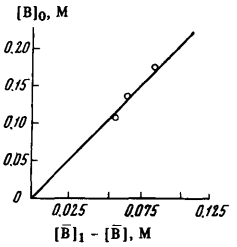


Figure 23. Dependence of difference between the steady-state concentrations of alcohols in experiments with supply of 1-phenylethanol ($[\bar{B}]_1$) and of pure ethylbenzene ($[\bar{B}]$) on concentration of 1-phenylethanol ($[\bar{B}]_0$) in solution supplied to vessel at 118°C, rate of flow 0.102 h^{-1}.

The variation in the steady-state concentration of the final product C, formed from B, with variation in the concentration of B in the solution fed to the vessel enables the rate of formation of C from B to be determined even if C is formed by several parallel routes. Actually, the rate of accumulation of C when the pure starting materials are supplied is

$$\frac{d[C]}{dt} = w_f^1 + k[RO_2^{\cdot}][\bar{B}] - \frac{u}{V}[\bar{C}] = 0$$

and when a solution of B is supplied to the system we have

$$\frac{d[C]}{dt} = w_f^1 + k[RO_2^{\cdot}][B]_1 - \frac{u}{V}[\bar{C}]_1 = 0,$$

where w_f^1 is the rate of formation of C from all products other than B. Hence the rate of formation of C from B is

$$k[RO_2^{\cdot}][B] = \frac{(u/V)([\bar{C}] + [\bar{C}]_1)[\bar{B}]}{([\bar{B}]_1 + [\bar{B}])} .$$

In this way the rate of formation of acetophenone (the final product in the oxidation of ethylbenzene in the absence of a catalyst[17,62]) from 1-phenylethanol has been calculated from the steady-state concentrations of acetophenone at various concentrations of the alcohol in the solution fed to the vessel, and oxidation of 1-phenylethanol has been shown[62] to be the only route by which the ketone is formed during the oxidation of ethylbenzene.

The mixture of reaction products often contains not only various functional derivatives but also a large number of isomeric products differing not only in the structure of the carbon skeleton but also in the position of the functional group in the molecule. When a reaction is conducted under static conditions it is extremely difficult to determine the rates of formation and consumption of each isomer, primarily because each such isomer must be isolated from the complicated mixture of reaction products. Conducting the process in an open system enables the rates of consumption of each of the isomers to be determined by analysing the total content of isomers in the system[64,65].

Let various isomeric products B_1, B_2, ..., B_n be formed in a reaction. It is required to determine the rate constant for consumption of a component B_k. Then for the total rate of accumulation of the isomers we have

$$\frac{d[B]}{dt} = \sum_{j=1}^{n} k_j[\bar{A}_j] - \sum_{\substack{i=1 \\ (i\neq k)}}^{n} k_i[RO_2^{\cdot}][\bar{B}_i] - k_k[RO_2^{\cdot}][\bar{B}_k] - \frac{u}{V}\sum_{\substack{i=1 \\ (i\neq k)}}^{n}[\bar{B}_i] - \left(\frac{u}{V}\right)[\bar{B}_k] = 0 \qquad (28)$$

When the isomer B_k is fed to the system at a concentration $[B_k]_0$, the steady-state concentrations of all isomers other than B_k remain unchanged, and the total accumulation of isomers will be described by the set of equations

$$\frac{d[B]}{dt} = \sum_{j=1}^{n} k_j[\bar{A}_j] - \sum_{\substack{i=1 \\ (i\neq k)}}^{n} k_i[RO_2^{\cdot}][\bar{B}_i] - k_k[RO_2^{\cdot}][\bar{B}_k]_1 + \frac{u}{V}\sum_{\substack{i=1 \\ (i\neq k)}}^{n}[\bar{B}_i] - \frac{u}{V}[\bar{B}_k]_1 + \frac{u}{V}[B_k]_0 = 0 . \qquad (29)$$

Subtracting Eqns. (28) from (29), we obtain

$$-k_k[RO_2^{\cdot}]\{[\bar{B}_k]_1 - [\bar{B}_k]\} - \frac{u}{V}\{[\bar{B}_k]_1 - [\bar{B}_k]\} + \frac{u}{V}[B_k]_0 = 0$$

$$k_k[RO_2^{\cdot}] = \frac{u}{V}\frac{-[\bar{B}_k]_1 + [\bar{B}_k] + [B_k]_0}{[\bar{B}_k]_1 - [\bar{B}_k]} = \frac{u}{V}\left\{-1 + \frac{[B_k]_0}{[\bar{B}_k]_1 - [\bar{B}_k]}\right\}$$

but

$$[\bar{B}_k]_1 - [\bar{B}_k] = \sum_{\substack{i=1 \\ (i\neq k)}}^{n}[\bar{B}_i] + [\bar{B}_k]_1 - \sum_{\substack{i=1 \\ (i\neq k)}}^{n}[\bar{B}_i] - [\bar{B}_k] = [\bar{B}_1] - [\bar{B}]$$

where $[\bar{B}]_1$ and $[\bar{B}]$ are the total concentrations of all the B isomers. Hence

$$k_k[RO_2^{\cdot}] = \frac{u}{V}\left\{-1 + \frac{[B_k]_0}{[\bar{B}]_1 - [\bar{B}]}\right\} .$$

The method was used to determine the reactivities of the isomeric decanols[65] in the oxidation of n-decane at 140°C. After a steady-state concentration of the alcohols had been established with pure n-decane supplied to the vessel (Fig. 24, curve *1*, section *1*), the supply was begun of n-decane containing 0.205 M decan-2-ol. After a new steady-state had been established (straight line *1*, *2*), the supply of decan-2-ol was terminated, and the supply was begun of a similar solution of decan-4-ol (straight line *1*, *3*), followed by decan-5-ol (*1*, *4*).

Since the steady-state concentrations of the total alcohols were the same with all three alcohols supplied to the

vessel, it could be concluded that all the decanols had the same reactivity towards the $RO_2^{\cdot}$ radical.

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The purpose of the present review was to examine the kinetics of reactions occurring in vessels having ideal mixing, and the opportunities which such systems present for studying the mechanism of complicated chemical reactions. Among a large amount of published information, therefore only those papers have been considered which make it possible to formulate or substantiate certain general features of open systems.

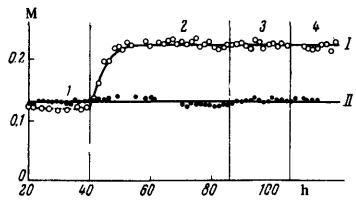


Figure 24. Steady-state concentrations of alcohols (I) and hydroperoxides (II) during the oxidation of n-decane in an open system at 140°C with a rate of flow of 0.0027 min^{-1}, during supply of: 1) n-decane containing no alcohol; 2) 0.205 M solution of decan-2-ol in n-decane; 3) 0.205 M solution of decan-4-ol in n-decane; 4) 0.205 M solution of decan-5-ol in n-decane.

Investigation of reaction kinetics in vessels having ideal mixing enables very important conclusions to be reached for the selection of reaction conditions for particular processes. Thus if the rate of accumulation of a product passes through a maximum, the maximum rate of the process can be permanently maintained by conducting it in vessels of ideal mixing. In this case the process is more suitably conducted in an open system than under static conditions[18,66].

Sometimes it is important to vary the reaction conditions during a process in order to obtain maximum yields, and this can be done especially conveniently by conducting the reaction in several vessels of ideal mixing connected in series. This procedure often enables the efficiency of a process to be increased considerably[66-70]. For example, in the sequence of processes

$$A + B \rightarrow X$$
$$X + B \rightarrow Y$$

represented in particular by chlorination, the product X is obtained in highest yield if the volumes of all the reaction vessels are the same. If primary and secondary products are formed by two parallel reactions of different order

$$2A + B \rightarrow X + Y$$
$$A + B \rightarrow Z$$

the highest yield of X is obtained by steadily increasing the volume from one reaction vessel to the next[18].

Most complicated reactions (consecutive and consecutive-parallel) involve many stages, each characterised by a definite activation energy, so that certain temperatures are required for the reactions. The possibility of varying the temperature during a process may lead to a very considerable increase in the yields.

The effect of variation in temperature has been demonstrated[18] for a model reaction represented by the scheme

$$\begin{array}{ccccc} A & + & B & \xrightarrow{2} & X \xrightarrow{4} Y \\ & & \downarrow 1 & & \downarrow 3 \\ & & P & & Q \end{array}$$

occurring in two reaction vessels of ideal mixing connected in series, Y being the required product. It was shown by calculation that, with the same temperature in the two reaction vessels, the yield of the final product cannot exceed 20–25%, whereas maintaining different temperatures in the two vessels makes it possible to increase the yield to 60%, i.e. by factors of 2.5–3.[18]

Another example of the favourable effect of change in temperature during a process is the catalytic oxidation of sulphur dioxide to sulphur trioxide[68,69]. If a definite degree of conversion (e.g. 97%) is specified, and the reaction is conducted in several vessels of ideal mixing connected in series and maintained at different temperatures, the quantity of catalyst used can be considerably diminished. In one reaction vessel of ideal mixing at 447.6°C the consumption of catalyst with 97% conversion is 0.633 m^3 h $kmole^{-1}$. If, however, the process is conducted in two series-connected reaction vessels, so that 92% conversion is achieved in the first vessel at 480°C, while in the second vessel complete oxidation of the dioxide to sulphur trioxide occurs at 447.6°C, the consumption of catalyst per kilomole of sulphur dioxide per hour with an overall degree of conversion of 97% is only 0.0577 m^3, i.e. one-eleventh.

In several cases it is extremely useful to conduct polymerisation processes in open systems. The constancy of the monomer concentration with time in an open system should lead to a narrower molecular-weight distribution[14,70], but, on the other hand, the unequal residence times of the polymeric species in the reaction zone tends to broaden the molecular-weight distribution. Which of these factors predominates will depend on the lifetime of the growing polymer chain.

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