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Gas-chromatographic Methods for Studying the Kinetics of Liquid-phase Reactions

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A brief account is given of the main features of chemical reactions occurring in the stationary liquid phase in gas-chromatographic columns during the pulsed injection of the sample. Attention is paid mainly to the use of direct and indirect pulse methods of gas chromatography for determining the kinetic characteristics of reactions in the liquid phase.
The advantages and limitations of these methods are analysed. A promising future is shown for the wide application of pulse gas-chromatographic methods for the experimental study of the kinetics of liquid-phase reactions.

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I. INTRODUCTION

Advances in the study of one of the main problems of modern chemistry—kinetics and the reactivity of chemical compounds—are governed in considerable measure by the development of new physicochemical methods and their wide practical incorporation in scientific investigations. Considerable progress in the study of the quantitative aspects of chemical reactions is due in particular to the wide use of gas-chromatographic methods in kinetic investigations [1,2].

Study of the composition of the reaction mixture is one of the most important tasks in experimental kinetic research. Although various physicochemical and chemical methods are employed to solve this problem, the most widely used techniques for analysing complicated multicomponent mixtures of volatile compounds are gas-chromatographic methods.

The simplest application of gas-chromatographic methods in research on kinetics consists in periodically withdrawing a sample of the reaction mixture from the reaction vessel, and then analysing it by gas chromatography. This is the mode of use adopted in most kinetic investigations.

An important characteristic of the chromatographic method is the possibility of studying the kinetics of a complicated chemical reaction at low degrees of conversion (under "pure" conditions), when the influence of the reaction products on the kinetics is negligible [3,4].

The first work on the application of gas chromatography to studying chemical kinetics by withdrawing and analysing samples of the reaction mixture was done during 1954–1956, [5-10] i.e. at the very start of the wide entry of gas chromatography into research practice. Gas chromatography is extensively used for studying the kinetics and the mechanism of chemical reactions because it possesses the following characteristics as an analytical method: (1) separation of the compounds under analysis is highly efficient (1000–5000 theoretical plates for packed columns, (20–100) × 10^3 theoretical plates for capillary columns); (2) the use of highly sensitive detectors enables small amounts of the reaction mixture (1–10 μl) to be employed for analysis, and the amount of component to be determined may be 0.01 mg for a catharometer and 10^{-4}–10^{-5} mg for a flame-ionisation detector; (3) the duration of an analysis is short, usually varying from a few minutes to several dozen minutes; and (4) standard chromatographic equipment is used for the separation.

In some studies of chemical conversion products, gas chromatography is used as a method of preparation, the compounds which are isolated on a preparative chromatograph being identified by other physicochemical methods [11]. Special mention must be made of the great opportunities for using gas chromatography in the analysis of radioactive and stable isotopes [12-15], which considerably extends the range of application of the method in kinetic investigations [12]. Methods have now been worked out for analysing the isotopes of hydrogen [14-18], the isotopes of oxygen [19], deuteriated methanes [20] and ethanes [21], and other labelled compounds [18].

By withdrawal of a sample from the reaction mixture and subsequent analysis, the gas-chromatography and the chemical process under investigation are isolated from one another, the former being used only as an efficient method of analysis. This method of applying gas chromatography to kinetics is by no means always the best, its wide use often being limited by several experimental difficulties: (1) kinetic investigations require the use as starting materials of pure compounds, and the amount of substance necessary for a kinetic experiment is often several grammes; (2) practical operation of the method is relatively simple only for slow reactions, rapid reactions requiring special methods to "freeze" the process; (3) gas chromatography can be used only to study the kinetics of reactions involving volatile components; and (4) the study of reactions occurring in viscous media is restricted by the difficulties involved in withdrawing the sample to be analysed and introducing it into the chromatograph.

Fundamentally new possibilities in studying the kinetics of reactions are opened up by pulse chromatographic methods, in which a plug of a volatile compound is injected into the carrier gas at the inlet to the reaction column, and the reaction occurring therein is assessed from the conversion or the retention time of the compound. In pulse methods the chemical reaction and the analysis are organically combined into a single method.

Two ways of applying pulse kinetic methods have been described, differing in the relation between the size of the plug of volatile reactant and the length of the active layer

in the reaction vessel. In the most widely used modification the plug is considerably smaller than the length of the layer, and in the other it considerably exceeds the length of the reaction vessel[22,23]. In the second variant there is practically no separation of the substances into individual zones along the layer. This method can be regarded as a microvariant of the usual flow technique for studying chemical reactions in a reaction vessel. We may mention also the possibility of using in kinetic investigations the method of reactant plugs, when reaction takes place in the reaction column between two plugs of volatile compounds, introduced successively into the column and moving along the reaction vessel at different speeds. In the literature the application of this method has been described only for analytical purposes[24].

In the kinetic study of reactions between a liquid and a volatile reactant (gas), investigation of the process under conditions of kinetic control is of especial interest. Various methods—e.g. vigorous shaking of the liquid phase in contact with the gaseous phase[25], bubbling the gas rapidly through the liquid[1], producing a thin layer of the liquid phase on the walls of the reaction vessel[26]—are used to accelerate diffusion processes in kinetic investigations of liquid-phase reactions in liquid–gas systems. When the reaction is conducted in a chromatographic reaction column, one of the reactants (the stationary liquid phase) is distributed as a thin layer (a few microns thick) on the surface of a macroporous inert carrier of surface $1-2\ m^2 g^{-1}$. On the assumption that blurring of the chromatographic zone is governed by the rate of mass exchange between gas and stationary liquid phase, the kinetic coefficient can be estimated by means of the relation[27] $\beta = 2\alpha/H$, in which α is the linear velocity of the carrier gas, and H the height equivalent to a theoretical plate. In practice we frequently have $\alpha \simeq 4\ cm\ s^{-1}$ and $H \simeq 0.2\ cm$, so that $\beta \simeq 40\ s^{-1}$. Thus it is probable that liquid-phase reactions having a rate constant $k \leqslant 1\ s^{-1}$ can be studied under kinetic conditions in a chromatographic reaction vessel.

Oxidation of an oil or other non-volatile product under the conditions of a chromatographic experiment, the liquid being applied as a thin layer to an appropriate porous carrier (glass, salt, metal), may be of interest for the rapid assessment of the working properties of technical products[28].

Pulse gas-chromatographic methods have been developed most widely and in greatest detail for the investigation of heterogeneous catalytic reactions. In several cases the results obtained can be used directly to examine the kinetics of liquid-phase reactions, for which gas-chromatographic methods are employed to a considerably smaller extent. Therefore the present review considers also work on the application of pulse gas-chromatographic methods to heterogeneous catalytic reactions where the results are of fundamental interest and can be used in studying liquid-phase reactions.

II. MAIN FEATURES OF CHEMICAL REACTIONS IN CHROMATOGRAPHIC COLUMNS

The pulse method was first suggested and employed by Kokes et al.[12] for the investigation of catalytic processes. Pulse chromatographic methods not only are more convenient and effective experimentally, but also provide fundamentally new opportunities for studying the kinetics and the mechanism of reactions.

A great contribution to the development of methods of reaction gas chromatography was made by Roginskii, Yanovskii, Gaziev, and their coworkers, who were the first to direct attention to the characteristics of chemical reactions occurring in chromatographic reaction vessels[29-35]. They showed that the kinetics of reactions occurring in chromatographic reaction columns are often so unusual that it is necessary in several cases to consider a special chromatographic régime of reactions, which differs fundamentally from the static and dynamic régimes.

For a reaction of the type $A \rightleftharpoons B + C$ with a pulsed supply of substance A to the reaction column, for example, the substances B and C are continuously generated and separated from A and from one another in zone A (the compounds A, B, and C move at different speeds along the reaction column), and form characteristic "peaks" outside the zone of the reactant A. Separation of reactant and products makes it possible to conduct the reversible reaction in one preferred direction, and to obtain yields of the desired product which considerably exceed the equilibrium yields under static conditions, etc. Under chromatographic conditions the chemical reaction takes place simultaneously (in conjunction) with chromatographic separation of reactants and products, which results in the process having the following characteristics: (1) owing to the separation it is mainly the initial reactant which is present in the reaction zone; (2) reversible reactions (e.g. of the type $A \rightleftharpoons B + C$) can be conducted predominantly in one direction, which enables yields to be obtained exceeding the equilibrium yields under static conditions; (3) the selectivity of the process is increased, the temperature of the reaction is lowered, side-reactions are eliminated, etc.; (4) the kinetic laws are simplified (e.g. the reaction zone contains practically no products which could act as poisons or promoters); and (5) new possibilities are opened up for studying the initial stages in the operation of a catalyst and for detecting intermediate products which are unstable under the reaction conditions[36].

If reaction of the initial volatile reactant is regarded as taking place in a system of coordinates moving at the speed of the reactant plug maximum in the reaction column, the reaction can be considered to occur in an open system in which the concentration of the initial volatile reactant continuously diminishes, and from which the reaction products are continuously removed (the rate of escape of the reaction products from the system is proportional to the difference between the velocities of the initial component and of the reaction products in the reaction column under the given experimental conditions). Reactions in open systems have several special characteristics[37]. In the present case an open reaction vessel of size proportional to the peak width of the initial reactant cannot be regarded as providing ideal mixing, since considerable concentration gradients of the reactants exist along its length. All this hinders an exact mathematical description of chemical reactions whose rate depends on the concentration of the products and the state of the catalyst.

Several specific physicochemical effects may occur during interaction between a solid catalyst and gases of variable composition, which are accompanied by a fundamental change in the results of the chemical process[38]. Continuous and pulsed supply of reactants produce different operating conditions for the catalyst, which may lead also to different results. In a study of the kinetics of the dehydrogenation of methanol[39], for example, similar results were obtained by the two methods. However, different kinetic parameters have been found[40] for the hydrogenation of acetone under conditions of pulsed and continuous reactant supply. Interesting results on the kinetics of the dehydrocyclisation of iso-octane and the hydrogenolysis of

mono- and di-alkylcyclopentanes have been obtained[41] by both methods, and a rational physical explanation is given of the observed differences for several types of reaction.

The above features of chemical reactions under pulse conditions are, of course, valid not only for catalytic but also for liquid-phase reactions. It must be emphasised only that, for the relatively wider range of liquid-phase chemical reactions, conducting the reactions in a chromatographic reaction column produces no change in the kinetics, as often occurs in the more complicated heterogeneous catalytic reactions.

In the case of slow irreversible reactions occurring in chromatographic columns, the zones of initial reactant and reaction products formed are now determined both by the chromatographic and by the kinetic characteristics of all the components in the reaction. For the reaction A → B, for example, the shapes of the zones due to the initial compound and to the product vary as a result of two processes—(1) ordinary chromatographic blurring during movement of the zone along the column, and (2) chemical reaction, during which the concentration of the initial compound in the chromatographic zone diminishes, while that of the reaction product increases.

Quantitative aspects of the formation of zones were discussed for the reaction A → B by Kallen and Heilbronner[42] on the basis of the theory of theoretical plates[43,44] within the framework of non-ideal linear chromatography. Equations were obtained[42] for the chromatographic zones of both the initial reactant compound and the product formed.

Let us examine the variation in concentration in the chromatographic zone of the initial reactant under conditions of equilibrium linear gas chromatography, caused by the action of longitudinal blurring factors. For a first-order reaction the initial equation can be written

$$\rho_G\frac{\partial c}{\partial t}+\alpha\rho_G\frac{\partial c}{\partial x}+\rho_L\frac{\partial a}{\partial t}+\rho_L k_L a=D^*\rho_G\frac{\partial^2 c}{\partial x^2} \qquad (1)$$

where ρ_G and ρ_L are the fractions of gaseous and liquid phases in a cross-section of the column, D^* is the quasi-diffusion coefficient of longitudinal migration, and k_L is the first-order reaction rate constant in the liquid phase.

In view of the linear relation between the concentration in the liquid phase a and that in the gas phase c, we eliminate the variable a from Eqn. (1):

$$\frac{\partial c}{\partial t}+v\frac{\partial c}{\partial x}+k_{eff}\cdot c=D_{eff}\frac{\partial^2 c}{\partial x^2}, \qquad (2)$$

where

$$v=\frac{\alpha}{1+\Gamma\frac{\rho_L}{\rho_G}}. \qquad (3)$$

$$k_{eff}=\frac{k_L}{\frac{\rho_G}{\rho_L}\cdot\frac{1}{\Gamma}+1} \quad (4) \qquad D_{eff}=\frac{D^*}{1+\Gamma\frac{\rho_L}{\rho_G}}. \qquad (5)$$

If no reaction occurs, $k_L = 0$, and Eqn. (1) becomes

$$\frac{\partial\tilde{c}}{\partial t}+v\frac{\partial\tilde{c}}{\partial x}=D_{eff}\frac{\partial^2\tilde{c}}{\partial z^2}. \qquad (6)$$

The solution of this equation is[27]

$$\tilde{c}=\frac{c_0}{\sqrt{4\pi D_{eff}\,t}}\exp\left[-\frac{(x-vt)^2}{4D_{eff}\,t}\right]. \qquad (7)$$

We shall seek a solution of Eqn. (1) in the form

$$c=f(t)\cdot\tilde{c}. \qquad (8)$$

Substituting Eqn. (8) in (1), and taking into account Eqn. (6), we obtain for $f(t)$

$$-\frac{df}{dz}=k_{eff}\cdot f(t). \qquad (9)$$

Hence an approximate solution of Eqn. (1) is

$$c=\frac{c_0}{\sqrt{4\pi D_{eff}\cdot t}}\exp-\left[\frac{(x-vt)^2}{4D_{eff}\,t}+k_{eff}\,t\right]. \qquad (10)$$

Analysis of this equation shows that the retention time of the zone maximum and the temporal width of the zone vary somewhat as a consequence of the chemical reaction. However, for the usual conditions of a chromatographic experiment and slow chemical reactions, this variation is small.

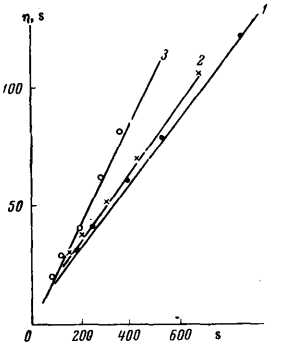


Figure 1. Dependence of peak width η on retention time for a mixture of hydrocarbons (in order of their elution from the column)—isopentane, pent-1-ene, isoprene, *cis*-piperylene, n-heptane— in a column (450 x 0.4 cm) containing as sorbent 10% of tritolyl phosphate and maleic anhydride (4:1) on a diatomite support at 70°C, with different velocities (ml min^{-1}) of the carrier gas: *1*) 31; *2*) 42; *3*) 65.

An experimental study has been made[45] of the blurring of the chromatographic zone of a reacting compound under the actual (non-equilibrium) conditions of gas–liquid chromatography. In order to ascertain whether this blurring is specific, the dependence of the peak width η on the residence time t in the column was determined simultaneously for the peaks due to a non-reactant and to a reactant[46]. It was supposed that, if the point (η_r, t_r) for the reactant did not lie on the $\eta = \eta(t)$ "calibration" curve obtained for non-reactant compounds, the specific blurring of the peak due to the chemical reaction could be estimated quantitatively; otherwise, it could be concluded that the reaction had no specific effect on the blurring of the chromatographic peak. Fig. 1 shows the dependence of peak width η on retention time for various hydrocarbons and various velocities of the carrier gas (31–65 ml min^{-1}). No specific blurring of the zone representing a reactant compound (isoprene) was detected (for constants of 5–16 $M^{-1}\,h^{-1}$ and degrees of conversion of 30–70%).

Roginskii and Rozental'[47] obtained a solution for the more general case in which a first-order homogeneous reaction in the gas phase and a heterogeneous catalytic reaction, of the first order with respect to the surface concentration of adsorbed reactant, occur simultaneously in the chromatographic reaction vessel. In this case the

reactant concentration distribution along the column should satisfy the set of equations

$$\frac{\partial p}{\partial t}+\frac{\partial a}{\partial t}+u\frac{\partial p}{\partial x}+k_1p+k_2a=0$$
$$\frac{\partial a}{\partial t}=k_3p-(k_2+k_4)a, \qquad (11)$$

where p is the number of reactant molecules per unit volume of the gas phase (which is proportional to the partial pressure of the reactant gas), x is the distance along the column from the point of entry of the gas into the column, a is the number of adsorbed reactant molecules per unit volume of the gas phase, u is the linear velocity of the carrier gas in the column, and k_1, k_2, k_3, and k_4 are the rate constants of the homogeneous reaction, the heterogeneous catalytic reaction, adsorption, and desorption respectively.

If the chemical reaction takes place in a film of the stationary liquid phase, the above set of equations and the consequent solution can be extended to reactions in gas–liquid chromatography, provided that $k_3=\beta$ and $k_4=\beta/\Gamma$, where β is the kinetic coefficient and $\Gamma=a/p$.

The partial pressure of the reactant gas before entering the column is a known function of time $\psi(t)$, with $\psi(t)=0$ at $t=0$ and $t\geqslant t_e$. At the inlet to the column $\psi(t)=p(x,t)$ at $x=0$.

If the time required to introduce the reactant gas into the reaction column t_e is close to zero, the solution obtained for the chromatographic zone of the reactant at $t-x/u\gg t_e$ was

$$p(x,t)=\frac{2xm_0k_3k_4\exp\left[(k_3-k_1-k_3+k_4)\frac{x}{u}-(k_3-k_4)tJ_1(z)\right.}{uz}, \qquad (12)$$

where

$$z=2\sqrt{k_3\cdot k_4\frac{x}{u}\left(t-\frac{x}{u}\right)}$$

m_0 is the initial quantity of reactant gas, and $J_1(z)$ is the first-order Bessel function of the first kind in an imaginary variable. For large values of the variable we have

$$J_1(z)=e^z/\sqrt{2\pi z}\ .$$

For values of x which satisfy the condition $x/u>3k_3k_4(k_2+k_4)$ the retention time of the reactant compound is given by the formula[47,48]

$$t_{max}=\frac{x}{u}+\frac{k_3\cdot k_4x}{2u(k_3+k_4)^2}\left[1+\sqrt{1-\frac{3u(k_3+k_4)}{k_3\cdot k_4x}}\right]. \qquad (13)$$

This equation shows that a homogeneous reaction does not affect the retention time.

A more general solution for the mean residence time of reactant molecules in a chromatographic reaction vessel and for the dispersion of the chromatographic zone has been obtained by Denisova and Rozental'[49]. These workers, in discussing first-order chemical reactions under pulse conditions, take into account the diffusion of gas molecules, and show that diffusion combined with the chemical reaction diminishes the mean residence time of unchanged molecules in the reaction vessel and also the width of the peak.

The characteristic kinetic laws for reactions of different orders ($n\neq1$) under conditions of pulse chromatography were first examined by Gaziev et al.[50] On the assumption that reaction occurs under conditions of ideal linear chromatography, they examined the diminution in concentration of the initial reactant for reactions of zero, first, and second orders and for pulses having different forms. In the case of a first-order reaction the degree of conversion was unaffected by the shape of the pulse, but for zero- and second-order reactions it does depend on the form of the pulse at the inlet to the reaction vessel.

The fact that the degree of conversion is independent of the form of the pulse for a first-order reaction under conditions of gas-chromatographic separation has received experimental confirmation[51], in which the degree of conversion of butadiene by reaction with maleic anhydride was determined from the areas of the peaks due to the reactant compound and from the heights of multistage peaks. In Fig. 2 the heights of the chromatographic zones (steps) preceding and following the reaction vessel (h_1/h_2) are plotted along the horizontal axis, and the ratio of the areas of the peaks (S_1/S_2) along the vertical axis. It is seen that the same results are obtained in the two cases: i.e. the form of the pulse does not affect the degree of conversion. In the study of first-order reactions, therefore, the degree of conversion can be measured by the ratio of peak areas, which is more convenient in practice.

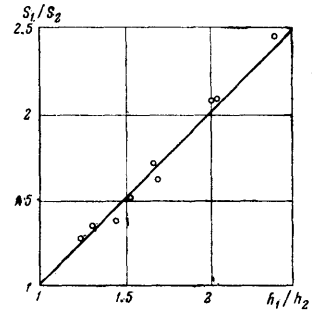


Figure 2. Dependence of S_1/S_2 on h_1/h_2 for butadiene at temperatures of 55.5°, 60°, and 74°C.

The field of application of the pulse gas-chromatographic method to liquid-phase reactions is considerably extended by using as a second reactant (the stationary liquid phase or a solution of a non-volatile component in it) a substance having a measurable vapour pressure at the temperature of the experiment. When the experiment is conducted under steady-state conditions, the loss of volatile substance from the column must be balanced by establishing the same concentration of this substance in the flow of carrier gas before the sample inlet. In this case reaction will take place in two phases—liquid and gaseous—and it is interesting to examine methods for determining separately the reaction rate constants in them. Assuming that the rates of chemical reaction can be described in both phases by a first-order equation, and that the reaction is kinetically controlled, let us examine the variation in the quantity of volatile substance (plug) resulting from passage through the reaction vessel, which is actually measured in an experiment. We remember that the superposition principle is satisfied (Eqn. 1):

$$W=\frac{dm}{dt}=\frac{dm_G}{dt}+\frac{dm_L}{dt}=F\rho_G\int_0^L w\,dx+F\rho_L\int_0^L w\,dx \qquad (14)$$

in which

$$w=k_Gc_B^lc \qquad (15)$$

$$w=k_La_B^na \qquad (16)$$

$$a=\Gamma c \qquad (17)$$

where k_G and k_L are the reaction rate constants in gas and liquid phases respectively, c and a are the corresponding concentrations of the volatile component, c_B and a_B are those of the second, less volatile component (practically constant under the experimental conditions), F is the cross-sectional area of the column, and ρ_G and ρ_L are the fractions of gas and liquid phases in the cross-section of the column. Let us rearrange Eqn. (14) to give

$$W = F[k_G\rho_G c_B^l + k_L a_B^n \Gamma\rho_L]\int_0^L cdx. \quad (18)$$

The total quantity of volatile component in the column satisfies the relation

$$\int_0^L cdx = \frac{m}{F(\rho_G + \Gamma\rho_L)} \quad (19)$$

and consequently

$$\frac{dm}{dt} = \frac{k_G\rho_G c_B^l + k_L a_B^n \Gamma\rho_L}{\rho_G + \Gamma\rho_L} \cdot m = k_{eff} \cdot m \quad (20)$$

where

$$k_{eff} = \frac{k_G\rho_G c_B^l + k_L\Gamma\rho_L a_B^n}{\rho_G + \Gamma\rho_L}. \quad (21)$$

Equation (20) is analogous to the differential rate equation for a first-order reaction.

Since, when detectors are used in the range of the linear scale, the quantity of substance is directly proportional to their area on the chromatogram, it follows that

$$\ln\frac{m_0}{m} = \ln\frac{S_0}{S} = k_{eff}\,t \quad (22)$$

where S_0 and S are the areas of the peak due to the volatile reactant on the chromatogram in the absence of the reaction vessel and after passing through it.

Let us make a more detailed examination of the equation for k_{eff}, having written it in the somewhat different form

$$k_{eff} = \frac{k_G\rho_G c_B^l/\rho_L + k_L\Gamma a_B^n}{\rho_G/\rho_L}. \quad (23)$$

All the terms in Eqn. (23) other than the rate constants can be determined. The separate determination of k_G and k_L requires that measurements should be made with different reaction vessels, characterised, for example, by different proportions of liquid and gaseous phases.

For stationary phases (reactants) which are either completely or nearly non-volatile, we note that $a_B \gg c_B$, and the first term in the numerator of Eqn. (21) can be neglected, so that

$$k_{eff} = \frac{k_L a_B^n}{\rho_G/\rho_L \cdot 1/\Gamma + 1}. \quad (24)$$

According to Ref. 27, we have

$$\rho_G/\rho_L \cdot \frac{1}{\Gamma} = \frac{t_0}{t_{corr}} \quad (25)$$

in which t_0 is the dead time of the reaction column and t_{corr} is the corrected retention time; therefore

$$\ln\frac{S_0}{S} = k_L a_B^n t_{corr}. \quad (26)$$

In the other extreme case, in which reaction takes place solely in the gas phase, and a flow of carrier gas containing a constant concentration of one reactant passes through a tube containing no sorbent, we find that

$$\ln\frac{S_0}{S} = k_G c_B^l t. \quad (27)$$

The theory of reversible chemical reactions of the type $A \rightleftharpoons B + C$ occurring under conditions of ideal linear chromatography in a column has been discussed by Magee [52]. A theoretical investigation of the effect of reaction velocity on the retention time and the form of the eluted peak has been made by Klinkenberg [53] for reactions of the type $A \rightleftharpoons B$. A closely related problem has also been analysed [54].

III. CHIEF EXPERIMENTAL METHODS FOR STUDYING THE KINETICS OF LIQUID-PHASE REACTIONS

The variation in concentration (quantity) of the components of a reaction can be studied by direct and indirect methods. In direct pulse chromatographic methods the rate of a chemical reaction is assessed from a direct determination of the quantity of a reacting component, and in indirect methods from the dependence of the retention parameters of unreactive components on the composition (quantity) of the reaction mixture used as the stationary liquid phase.

Table 1. Various forms of pulse gas-chromatographic methods for studying the kinetics of chemical reactions.

Reactants volatile	One reactant volatile, others non-volatile	All reactants non-volatile
1. Two volatile components enter reaction column together. Method has been used to study the kinetics of catalytic reactions [55]. 2. One component injected as plugs into reaction column, while the second enters the reaction vessel continuously in the stream of carrier gas. Method suggested in Ref. 50. 3. Plug of one component injected into reaction column, and after a definite time interval a plug of the second component. Reaction occurs during the time in which the second overtakes the first component in the reaction column.	4. Volatile component injected into column in plugs, while non-volatile compounds used as stationary liquid phase, either directly [56] or as solution in non-volatile solvent [51]. 5. Volatile component introduced continuously into column, while non-volatile components used as stationary liquid phase. Into the reaction column are periodically injected plugs of a standard mixture of non-reactants, the variation in whose retention times indicates the composition of stationary liquid phase (indirect method) [58].	6. Starting materials used as stationary phase in reaction column. Plugs of mixture of standard non-reactants periodically injected into column, the variation in their retention times indicating the variation in composition of the stationary liquid phase resulting from reaction (proposed [58] indirect method).

Pulse chromatographic methods of kinetic investigation are applicable to various chemical reactions, but the choice of the optimum method depends on the state of aggregation and the volatility of the reaction components, as well as on the type of reaction. Some of the main modifications of the method for reactions of the type $A + B + \ldots \rightarrow C + D + \ldots$ are listed in Table 1. It can be seen that pulse gas-chromatographic methods can be successfully applied to a wide range of reactions, the components of which are in various states of aggregation. It must be stressed that Table 1 indicates only the chief variants: for example, it does not reflect experimental methods of using volatile products to study the kinetics of non-volatile compounds, which are especially promising for the kinetic examination of the degradation of polymers.

The arrangement of the kinetic chromatographic apparatus is varied depending on the method of kinetic study and the type of reaction. Table 2 gives some of the principal block diagrams. Switching devices (valves, multiway taps, etc.) are not shown in these diagrams.

Table 2 illustrates four main types of scheme, differing in the relative arrangement of chromatographic column and reaction vessel. When it is necessary to work with labelled atoms, these schemes must be supplemented by detectors to record the labelled compounds (e.g. Geiger counters).

Table 2. Some fundamental block schemes for studying the kinetics of chemical reactions.

Chromatographic schemes	Characteristics of scheme
1	Simple chromatographic scheme. Column is also reaction vessel.
2.1 2.2 2.3 2.4	Reaction vessel preceded by chromatographic column, which is used to obtain a plug of the pure reactant. Trap used if necessary to constrict plug of initial volatile reactant. Column and reaction vessel may be located in different thermostats. The most universal scheme of this type is 2.4.
3.1 3.2	Reaction vessel followed by column to separate initial reactants and reaction products.
4	Combined scheme, enabling pure substances to be obtained before entering the reaction vessel, and substances to be analysed after leaving it.

○ 1 ⋀⋀⋀ 2 □ 3 △ 4 ⊠ 5 ● 6

Conventional symbols: *1*) device for injecting sample; *2*) chromatographic column; *3*) detector having two measuring cells; *4*) measuring unit with pen-recorder; *5*) reaction vessel; *6*) trap.

In the design of chromatographic apparatus for kinetic studies account must be taken of the following possibilities in conducting an experiment—(1) "preparative" (in analytical quantities, of the order of milligrammes and fractions of a milligramme) chromatographic production of the pure initial reactant, (2) mixing of one initial reactant with others, (3) injection of the reaction mixture as a sharp plug (instantaneous introduction) or as a rectangular pulse of finite duration (step), or else continuous introduction of one or more reactants into the reaction vessel, (4) chromatographic separation of the reaction products and determination of their concentration both before and after the reaction, and (5) stabilisation of the reaction conditions (temperature, rate of flow of carrier gas, etc.).

An important advantage of direct pulse gas-chromatographic methods for studying the kinetics of liquid-phase reactions is the possibility of using impure substances as starting materials, these being separated from impurities by chromatography immediately before the reaction. This increases both the reliability and the universality of the method. Rephrasing Ostwald's well known statement, we can say that pulse chromatographic methods enable accurate results to be obtained when using contaminated starting materials.

It may be noted that kinetic chromatographic equipment can be assembled very quickly by using standard parts (thermostats, detectors, columns, measuring devices, etc.) of gas chromatographs.

IV. DIRECT PULSED CHROMATOGRAPHIC METHODS FOR STUDYING THE KINETICS OF LIQUID-PHASE REACTIONS

A direct method for the kinetic study of liquid-phase reactions was first used by Gil-Av and Herzberg-Minzly in investigating the reaction of conjugated dienes with chloromaleic anhydride[56]. A plug of the diene was introduced into the flow of carrier gas before the latter entered the reaction column (dimensions 200 × 0.4 cm) containing the chloromaleic anhydride. It was shown that the reaction was not controlled by diffusion, and corresponded to a first-order kinetic equation. From measurements of the rate constants at two temperatures (25° and 40°C) the activation energy was found to be 17.2 and 15 kcal mole^{-1} for *trans*-penta-1,3-diene and isoprene respectively, these values agreeing with published data.

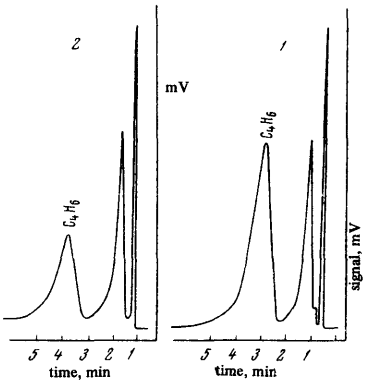


Figure 3. Chromatograms of butadiene:
1) preceding the reaction vessel; *2*) following the reaction vessel.

This method has been developed[51] to determine the order of reaction with respect to a second, non-volatile component and the rate constant of a bimolecular reaction. Scheme 2.2 in Table 2 was used for the experimental work, in which the kinetics of the reaction between dienes and maleic anhydride was studied. Fig. 3 shows as example the chromatograms of butadiene before and after reaction with maleic anhydride. The peaks eluted from the column before the butadiene are due to air and butenes present as impurities in the butadiene. The second component in the reaction—maleic anhydride—was deposited on brick as a solution in tritolyl phosphate saturated at 45°C. This choice of solvent had the aims of—(1) extending the temperature range of the reaction (since the melting point of maleic anhydride is 55°C, so that it cannot be used as a reactant in the liquid phase below this temperature), (2) increasing the retention time and hence the period of contact of the reactants, and (3) investigating the kinetics of the reaction with respect to the non-volatile component, i.e. maleic anhydride.

The kinetic measurements were made at a constant concentration of maleic anhydride, which exceeded by factors of 10^2–10^4 that of the volatile component, butadiene. Not more than 0.02% of the maleic anhydride reacted during one experiment. Reaction in the gas phase had no appreciable effect on the observed results. Kruglikova and the Reviewer have shown that, for this reaction at 69°C, $k_G\rho_G c_B/k_L\Gamma\rho_L a_B \simeq 10^{-4}$, so that the gas-phase reaction can be disregarded.

Degree of conversion was determined from the change in the areas of the chromatographic peaks preceding and following the reaction vessel. The slight blurring which occurs when the plug of the substances passes through the reaction vessel should not affect the results, since with a first-order reaction the relative conversion does not depend on the form of the plug. The bimolecular rate constant was calculated by means of Eqn. (26), the concentration a_B being varied[57]. This equation was used to determine the kinetic characteristics of the Diels–Alder reaction of butadiene, isoprene, and penta-1,3-diene with maleic anhydride. Under the given conditions these reactions are practically irreversible[59].

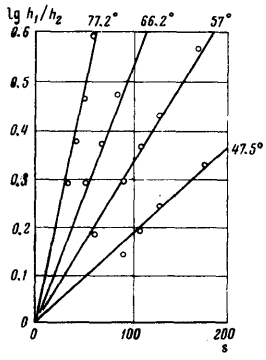


Figure 4. Dependence of logarithm of degree of conversion of butadiene on time of reaction at various temperatures.

Fig. 4 shows the dependence of the logarithm of the degree of conversion of butadiene on its contact time with maleic anhydride at various temperatures. The contact time of the reactants was calculated as the difference between the retention times of the diene preceding and following the reaction vessel, with the dead time of the latter taken into account. The straight lines obtained confirm that, with a constant concentration of maleic anhydride, the reaction obeys a first-order equation with respect to the diene.

The order of the reaction with respect to maleic anhydride can also be determined by this method. For this purpose different concentrations of maleic anhydride in tritolyl phosphate were used in a series of experiments, and the logarithm of the maleic anhydride concentration $\lg c_{MA}$ was plotted against $\lg y$, where $y = \lg(S_0/St_{corr})$. Fig. 5 illustrates this relationship for the reactions of maleic anhydride with butadiene and with isoprene. The slopes of these straight lines show that the order of the reaction with respect to maleic anhydride differs slightly from unity (slightly greater with butadiene, and slightly less than unity with isoprene), which is probably due to the influence of the solvent used.

The activation energies of the reactions were determined graphically from the linear dependence of the logarithm of the rate constant on the reciprocal of the temperature. Activation energies were evaluated by this method for the reactions of butadiene, isoprene, and piperylene with maleic anhydride. Table 3 gives values determined by the pulse chromatographic method for the rate constants and the activation energies of these reactions, and includes for comparison available published values of the activation energies calculated from the quantity of diene remaining unchanged, as in the case of a second-order reaction[60]. The rate constants differ somewhat from the published values, but are of the same order of magnitude, while the activation energies for butadiene and isoprene are practically identical with the published values. The results in Table 3 are mean values for whole series of experiments. Individual values of the constants do not differ from their mean value by more than 10%. Thus rate constants and activation energies for bimolecular reactions can be determined quite accurately by the pulse chromatographic method.

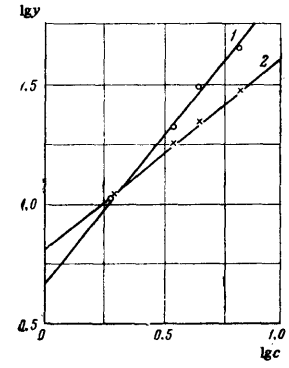


Figure 5. Dependence of lg$y$ on lg$c$ for: *1*) butadiene; *2*) isoprene.

Table 3. Rate constants and activation energies for reactions of dienes with maleic anhydride.

Diene	Reaction rate constants k, $M^{-1}\,h^{-1}$, at temperatures (°C)										Activation energy, kcal mole^{-1}	
	47.5	49	51.3	57	59.6	60.5	66	68.3	69.6	77	found	Ref. 60
Butadiene	1.55			2.8			4.7			7.9	12±0.8	11.7±0.8
Isoprene		5.75			11.0			16.9			12.1±1	12.2
Piperylene			8.5			12.4			16.7		8.1	—

The rate constants of these reactions can be determined on chromatographic apparatus having a single detector if the reactant concentration is measured relative to an unreactive reference substance introduced into the mixture:

$$k_L = \frac{2.3 \lg \dfrac{S_{01}/S_{1ref}}{S_{02}/S_{2ref}}}{c_B^n t_{L\,corr}} \qquad (28)$$

where S_{01}/S_{1ref} is the ratio of the areas of the chromatographic peaks for the diene and the reference material on the column (in the absence of the reaction vessel), and S_{02}/S_{2ref} is the corresponding ratio when a reaction column

is used. Rate constants obtained by this method for the reaction of isoprene with maleic anhydride are practically identical with results obtained by other methods.

Pulse methods can be applied also to studying the kinetics of isotopic exchange. They have been used[61] to produce deuterium-labelled compounds (ketones containing a labile hydrogen atom) on a semi-preparative scale. The compound labelled with deuterium was formed during passage of a plug of the volatile compound through a gas–liquid chromatographic column filled with Gaschrom Z (100–120 mesh) which had been coated with 10% Carbowax 6000 and 10% potassium deuteroxide KOD. The column (3 m long) was used for the semi-preparative production of deuterated compounds after the initial injection of 0.3 ml of D_2O and stabilisation for a few hours. A table is given[61] indicating the conditions of deuterium exchange and the degree of exchange.

A pulse chromatographic method has been used also to study the kinetics of the esterification with acetic anhydride of various alcohols having high boiling points[62]. The volatile reactant (acetic anhydride) entered the reaction vessel in the form of a plug, while the non-volatile reactant (the alcohol) was present in the reaction column as the stationary liquid phase. In contrast to the application of the pulse method to diene syntheses, in the esterification of an alcohol with acetic anhydride one of the reaction products (acetic acid) is eluted from the reaction column after the initial component (acetic anhydride).

The reaction vessel used was a chromatographic column of size 100 × 0.4 cm. The non-volatile alcohol was deposited on fluorinated plastic A (1 : 10 by weight). The purity of the initial alcohols was checked chromatographically. Esterification of the alcohols was studied over the temperature range 80–130°C, since the rate of esterification is small at lower temperatures, and at higher temperatures the alcohols begin to volatilise appreciably from the column.

Table 4. Kinetic characteristics of the esterification of alcohols with acetic anhydride.

Reactant	Rate constants		Activation energy, kcal mole^{-1}
	first order k_I, min^{-1}	second order k_{II}, M^{-1} h^{-1}	
Dodecan-1-ol	1.12*	14.8*	17
Hexadecan-1-ol	0.73**	12.9**	19
Heptadecan-9-ol	0.099**	1.9**	24
Cyclododecanol	0.22**	3.0**	15
7-Methyltridecan-7-ol	0.041*	0.65*	23

* At 104°C. ** At 100.7°C.

A mixture of acetic anhydride and the reference material (benzene) was introduced as plugs into the chromatographic reaction column, where the test alcohol was used as the stationary liquid phase. Different degrees of absorption of the acetic anhydride were obtained by varying the speed of the carrier gas. The time of contact of the reactants was determined as the difference between the retention time of the acetic anhydride and the dead time of the reaction column.

The first-order rate constants with respect to acetic anhydride were determined by the method of least squares from the linear dependence of $\lg(S_0/S_{ref})$ on the period of contact.

Table 4 shows that primary alcohols have the highest esterification rate constants, while tertiary alcohols are esterified much more slowly under the same conditions, secondary alcohols occupying an intermediate position with respect to their reactivity. The activation energies of these reactions were determined from the temperature dependence of the rate constants, and are included in Table 4.

The above examples indicate the promising future for the wide application of direct pulse methods in the kinetic study of liquid-phase reactions.

V. INDIRECT PULSED CHROMATOGRAPHIC METHODS FOR STUDYING THE KINETICS OF CHEMICAL REACTIONS

The above methods for studying the kinetics of liquid-phase reactions cannot be used with reactions involving only compounds which are non-volatile or which are unstable at high temperatures, i.e. compounds for which direct gas-chromatographic analysis is impossible under the reaction conditions. However, analysis is often a complicated problem for such systems.

A new form of gas chromatography—inverse gas chromatography—has been used to study the kinetics of chemical reactions in such systems[63,64]. In contrast to the usual form of development chromatography, the substance to be analysed is the stationary liquid phase, and a mixture of known standard compounds of various types is separated on it. In inverse chromatography the substances and mixtures under analysis (stationary liquid phases) are characterised mainly by the retention parameters of the components of the standard mixture. The stationary phase (test compound) is characterised by a spectrum of retention parameters of the standard compounds. The method can be applied both for group identification and for determining the quantitative composition of simple mixtures[63,64].

In a proposed method[58] for studying chemical kinetics, the reaction occurs in the chromatographic column, and the reaction mixture is used as stationary liquid phase for a standard mixture of non-reactants. Variation in the composition of the reaction mixture with time is checked by periodic measurement of the elution characteristics (e.g. the relative retention times) of the non-reactants. Thus determination of the composition of the reaction mixture is based on a relation of the type

$$c_i = f(\tau_j) \qquad (29)$$

where c_i is the concentration of one of the components in the reaction mixture, and τ_j is the relative retention time of a standard non-reactive compound. The inverse relation $\tau_j = \psi(c_i)$ has been studied by several investigators in connection with the problem of using binary mixed liquid phases for separating complicated mixtures of volatile compounds[65–68].

Results given in most of the papers indicate a linear relation between the relative retention parameter and the concentration of one of the components in the binary stationary phase. In general, however, this relation must be regarded as non-linear, which was correctly pointed out in Ref. 68.

If some physical property (in the present case the retention time τ) is proportional to the concentration of a substance in the reaction mixture, we have

$$\tau = \tau_\infty + (\tau_0 - \tau_\infty)\frac{c}{c_0} \qquad (30)$$

where τ, τ_0, and τ_∞ are the retention times of some substance on the reaction mixture (the stationary liquid phase)

respectively at time t, at the start of the reaction, and when the reaction is complete. In this case the kinetic equation for a unidirectional first-order reaction can be written[37]

$$k = \frac{2.3}{t} \lg \frac{\tau_0 - \tau_\infty}{\tau_t - \tau_\infty} \quad . \qquad (31)$$

The indirect pulse method of studying kinetics has several advantages: it does not require the removal of samples, and only small amounts of the test substances are needed, of the order of a few milligrammes in the case of capillary columns; it can be used to investigate the kinetics of reactions in systems which cannot be analysed chromatographically because of thermal instability or non-volatility; and it enables kinetic investigations to be made in various systems—solid–liquid, liquid–liquid, liquid–gas—and also for various catalytic reactions.

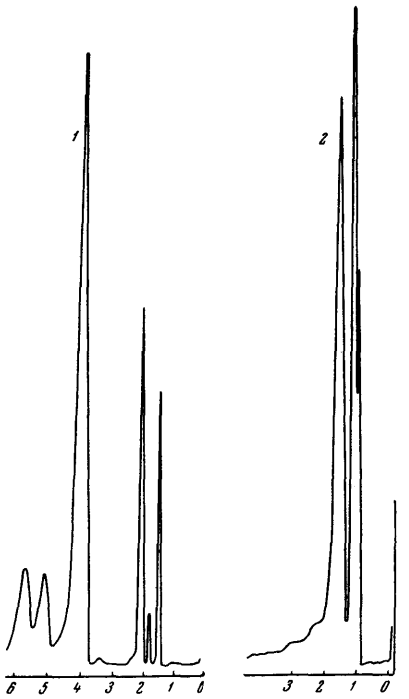


Figure 6. Chromatograms of standard mixture of butenes on: *1*) original benzaldehyde; *2*) completely oxidised benzaldehyde.

An example of the use of this method is the kinetic investigation of the oxidation of benzaldehyde to benzoic acid. The usual chromatographic apparatus was used for the kinetic study[69]. Air was passed at a rate of 30 ml min^{-1}, to act both as oxidant and as carrier gas, through a chromatographic column (200 × 0.4 cm) filled with diatomaceous brick on which had been deposited benzaldehyde (40%). Since the oxidation of benzaldehyde is catalysed by traces of heavy metals, the brick had first been impregnated with a solution of copper sulphate (0.1%). The benzaldehyde had been applied to the brick from acetone solution in an atmosphere of nitrogen freed from oxygen. The standard mixture comprised ethane, propene, but-1-ene, and but-2-ene, since these compounds were characterised by different retention times on benzaldehyde and benzoic acid. The procedure consisted in obtaining chromatograms of the standard mixture on the reaction mixture (benzaldehyde + benzoic acid) after definite intervals of time. The retention times of the compounds changed as the benzaldehyde was oxidised.

Chromatograms obtained on the original benzaldehyde and on the completely oxidised compound show (Fig. 6) a marked change in the retention times. At 0°C the concentration of benzoic acid in benzaldehyde corresponding to saturation is 7%, so that the composition of the liquid phase then remains practically constant during the oxidation, while the quantity of benzaldehyde (stationary liquid phase) decreases. During oxidation the corrected retention times vary in direct proportion to the content of benzaldehyde in the column. Therefore Eqn. (31) can be used in processing the experimental results, on the assumption that the kinetics of the oxidation of benzaldehyde to benzoic acid in the presence of oxygen corresponds formally to a first-order equation. The effective rate constant calculated by means of Eqn. (31) is 4.7×10^{-3} min^{-1}.

The results of the proposed method for studying the kinetics of the oxidation of benzaldehyde have been compared with those obtained by oxidation in a bubbler reaction vessel. These gave an oxidation rate constant of 4.6×10^{-3} min^{-1}. Thus the proposed chromatographic method of studying reaction kinetics gives results in good agreement with those obtained by a method of bulk oxidation.

The method under discussion can be applied not only to binary systems: in the case of multicomponent systems it is possible to select volatile compounds whose retention times would be greatly dependent on the content of individual components in the liquid phase.

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In conclusion we may note that the development of pulse gas-chromatographic methods is far from complete. An especially interesting application, it seems to us, is their development for study of the mechanism of liquid-phase reactions and of the effect of the medium on the rates of chemical changes. However, the experience which has now accumulated is sufficient for the wide application of pulse methods in the practical investigation of various liquid-phase reactions.

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