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Stopped Flow and Reversed Flow Gas Chromatography

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The application of stopped flow and reversed flow gas chromatography to the study of the kinetics of slow chemical and physical processes in chromatographic column-reactors and also to the solution of a number of analytical problems is examined. It is shown that stopped flow and reversed flow gas chromatography should be regarded as a variety of headspace analysis in chromatographic column-reactors or in microreactors incorporated in a single chromatographic system.
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I. INTRODUCTION

The advances achieved recently in the study of chemical reactions in chromatographic column-reactors have been determined to a large extent by the development of methodology and experimental technique. A number of communications and chapters in monographs published in recent years have been devoted to the application of chromatographic methods to the study of the kinetics and mechanisms of reactions on the surface of an adsorbent-catalyst or in solution in the stationary phase.[1-5] However, certain recently proposed methodological procedures are either discussed too briefly and incompletely in the above communications or are not considered at all.

This review deals with the application of stopped flow gas chromatography (SFGC) and reversed flow gas chromatography (RFGC) to the study of a number of slow chemical and physical processes and also to the solution of a number of analytical problems. From our point of view, SFGC and RFGC should be regarded as a variety of the headspace analytical method,[6-8] which combines many of the modern chromatographic methods based on the gas extraction of volatile compounds from condensed liquid or solid phases.[9] Two main groups of headspace analytical methods are known:[7,8] (1) the static methods where the gas and condensed phases in contact form a closed system; (2) the dynamic methods where the phases come into contact in an open system and the gas is blown through a layer or over a layer of liquid or a granulated solid phase. In the various analytical and physicochemical applications of headspace analysis, a combination of the static and dynamic versions is frequently employed and contact between the phases is usually achieved in autonomous vessels having a constant volume (flask, bottle) or a variable volume (syringe), which are not elements of a single gas circuit of the chromatograph. The specificity of the SFGC and RFGC methods consists in the fact that the gas extraction of volatile organic compounds from stationary solid or liquid phases takes place directly in the chromatographic column-reactors or in microreactors incorporated in a single chromatographic system.

II. STOPPED FLOW GAS CHROMATOGRAPHY

The gas-chromatographic method for the study of sorption processes and chemical reactions with periodic arrests of the carrier gas flow was proposed in 1967 by Phillips and co-workers.[10-12] A fairly rigorous theory of the method, dealing with the set of diffusion, sorption, and desorption phenomena and also with chemical reactions at the active centres of the adsorbent-catalyst and the distribution of the reactant and products between the stationary and mobile phases under equilibrium and non-equilibrium SFGC conditions, was developed by Katsanos and co-workers.[13-15] The method has been described briefly in a number of communications.[1-4]

Phillips and co-workers[10-12] gave the name stopped flow chromatography to the proposed method which has now been firmly established in the English language literature (the term "stop-flow chromatography" is sometimes encountered). It is in keeping with the term "stop-flow spectrophotometry", known in Russian as "metod ostanovlennoi strui".[16] However, the stopped flow method has been developed for spectrophotometric studies of very rapid chemical reactions and is based on completely different principles and it is therefore illegitimate to employ the phrase "gazokhromatogorafi-cheskii metod ostanovlennoi strui" as the Russian translation of the term "stopped-flow chromatography" (see the Russian resume in Lycourghiotis's paper[17]).†

In the early analytical gas chromatographic practice, arrests of the carrier gas flow were employed in connection with the application of combined separation and detection methods even before the introduction of SFGC but for quite different purposes. This concerns the "interrupted gas chromatographic" method in which provision is made for the arrest of the carrier gas flow every time when the compound eluted from the separating column enters the cell of an insufficiently rapidly responding detector or in the combustion tube for the measurement of the IR or mass spectra, the measurement of radioactivity, or elemental analysis.[18-23]

We may note that many schemes proposed[18-23] for gas circuits can be used successfully also in SFGC. Certain versions of these schemes will be considered below.

1. Principles and Applications of the SFGC Method

The traditional eluent gas chromatography is based on the continuous extraction of the compounds to be determined by the carrier gas from the stationary liquid or solid phases. The method has been used successfully for the solution of numerous analytical problems and for the physicochemical

†The Russians use a phrase which can be translated as "gas chromatographic method with arrests of the carrier gas flow" (Ed. of Translation).

study of the processes occurring in the chromatographic column-reactors at sufficiently high rates. If a slow physical or chemical process with evolution of a volatile compound into the gas phase takes place in the column, then the chromatographic output curve for reaction systems characterised by strong retention of the reactants and weak retention of the reaction products, under the conditions of a traditional eluent gas chromatography, has the form illustrated in Fig. 1*a*. The asymmetry of the product peak is in this case due to the fact that the rate of the process investigated is lower than the rate of extraction:

$$k_r \ll k_e, \qquad (1)$$

where k_r is the reaction rate constant and k_e the extraction rate constant.

When the flow of carrier gas is stopped for a fixed time Δt, the dynamic gas extraction regime is transformed into a static regime. The volatile organic substances evolved from the stationary phase accumulate in a limited volume in the mobile phase in an amount sufficient for their detection in the form of narrow and symmetrical peaks (Fig. 1*b*) when the gas flow is subsequently restarted. The virtually identical degrees of spreading of the product bands after different arrests facilitates their identification in those cases where the impurities present in the reagent are eluted from the column. The procedure involving the repeated and consecutive stopping and restarting of the carrier gas flow for a rigorously fixed period (as a rule 1–2 min) makes it possible to measure the change in the concentration in substance B as a function of time. This distinguishes the present method from the majority of others in which the concentrations of the reactant or product thermselves are measured and not their changes.

An important advantage of the method consists in the possibility of using it to investigate reactions which lead to several products. If, for example, not one but two products are formed, traditional eluent chromatography can only indicate their formation (the break in the chromatographic output curve in Fig. 2*a*), while with the aid of SFGC it is possible to follow the changes in the ratio of the product concentrations as a function of time (Fig. 2*b*), to investigate the multistage process mechanism, and to obtain information about the comparative activities of the catalysts.

A distinctive feature of the SFGC method is the possibility of following in one experiment the course of the chemical reaction over a wide range of reactant conversions starting from very low and continuing up to very high (99.5%) degrees of conversion.[11]

At the present time many slow physical processes and chemical reactions in chromatographic column-reactors have become the objects of systematic study with the aid of SFGC: dehydration of alcohols,[11,12,17,24,25] dehydrohalogenation of alkyl halides,[10–12,26–29] deamination of aliphatic and alicyclic amines.[17,30–33] hydrocracking of paraffinic hydrocarbons,[34] hydrogenolysis of aliphatic aldehydes,[35] hydrogenation of aliphatic ketones,[36] deuterium exchange,[37] isomerisation of n-butenes,[38] adsorption and desorption of n-heptane in carrier gas–modified Al_2O_3 or porous glass systems,[39] and diffusion of ethylene, propene, and diethyl ether molecules in nitrogen.[40]

Together with the physicochemical applications, interesting possibilities of using SFGC for analytical purposes have been discovered (see below).

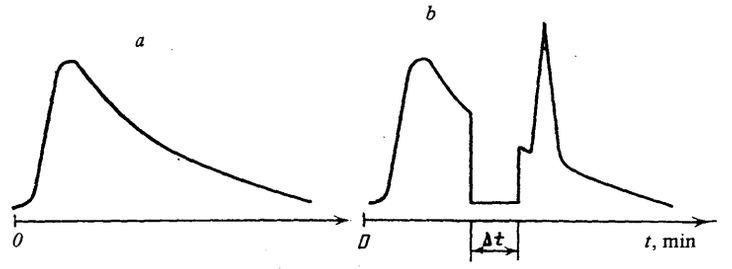


Figure 1. Approximate form of the chromatographic output curves for the reaction A → B in the column-reactor under the conditions of traditional eluent gas chromatography and gas chromatography with a single arrest of the carrier gas (for explanations, see text).

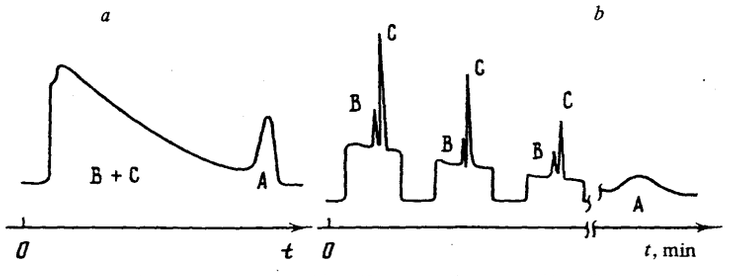


Figure 2. Chromatographic output curves for the reaction A → B + C in the column-reactor:[11] *a*) traditional eluent chromatography; *b*) SFGC.

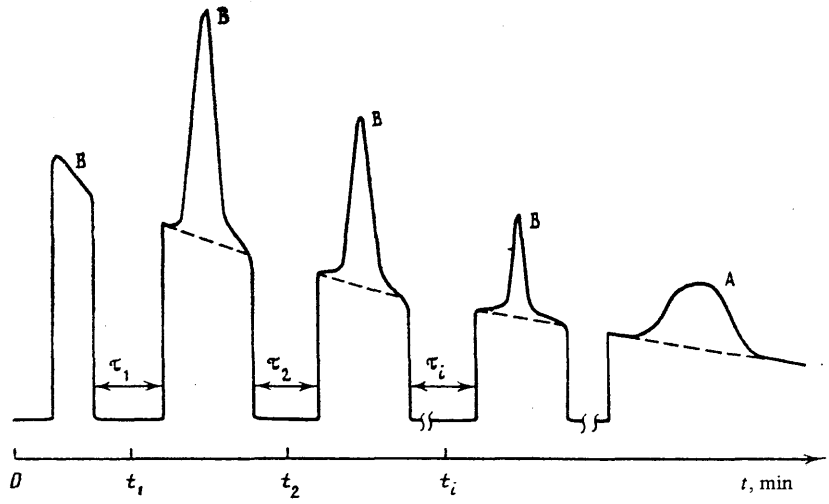


Figure 3. Typical chromatogram illustrating the possibilities of the SFGC method in the study of the kinetics of the first order chemical reaction A →B in the column-reactor (for explanation, see text).

2. Determination of the Rate Constants for Chemical and Physical First Order Processes

Phillips et al.[10] examined the possibility of investigating the kinetics of four types of first order chemical reactions by the SFGC method.

1. Isomerisation of A to B:

$$A \xrightarrow{k} B, \qquad (2)$$

2. Decomposition of A with formation of one (B) or several products:

$$A \xrightarrow{k} B + C + \ldots \qquad (3)$$

3. The formation from A of two (for example, B and C) or more products via independent parallel pathways:

$$A \begin{cases} \xrightarrow{k_B} B \\ \xrightarrow{k_C} C \end{cases} \qquad (4)$$

4. Consecutive conversion of A into B and then of B into C:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (5)$$

The initial approach to the interpretation of the experimental results[10–12] was based on the model of linear and ideal chromatography, which was itself based on two important assumptions: the constancy of the partition coefficients of the compounds eluted in the course of the experiment and the instantaneous establishment of equilibrium between the phases in the column-reactor. It was also assumed that the surface of the adsorbent-catalyst contains centres with identical catalytic activities and that, when the carrier gas flow is interrupted, the chemical reaction proceeds under rigorously static conditions. In this case, when the flow of the carrier gas is restarted, one records the so called "stop-peak", whose area is rigorously proportional to the amount of product formed during the arrest.

It has been suggested that the rate constant for the reversible first order reaction (2) be found from the equation

$$k = [\ln(P_i\tau_i/P_i\tau_1)]/f(t_i - t_1) \qquad (6)$$

where P_1 and P_i are quantitative parameters (the areas or heights) of the first and *i*th "stop-peaks" respectively, τ_1 and τ_i are the durations of the first and *i*th arrests respectively, t_1 and t_i are the instants corresponding to the centres of the first and *i*th arrests respectively, and f is the fraction of reactant molecules sorbed by the active centres on the surface.#

If the product $kf\tau$ is fairly large (exceeds 0.3, which is rarely observed in the experiment), the rate constant is found from the equation

$$k = \{\ln[P_1 \sinh(kf\tau_i)]/P_i \sinh(kf\tau_1)]\}/f(t_i - t_1). \qquad (7)$$

In order to increase the accuracy of the calculation, it has been recommended[10] that the areas (or heights) of the most remote "stop-peaks", referring to the beginning and end of the reaction (Fig.3), be compared and that the calculation from the intermediate parameters (for close values of T) be carried out only in order to estimate the stability of the operation of the column-reactor and to find the order of the reaction.

#The numerical values of f are determined by the ratio $[t'_{RA}/t_M) - 1]t_M/t'_{RA}$, where t'_{RA} is the corrected retention time of the reactant and t_M the dead time. In the majority of cases f is close to unity (0.985–0.987). When the direct experimental measurement of t'_{RA} is impossible, it can be found indirectly.[29]

We emphasise that, in the derivation of Eqns.(6) and (7), the duration of the arrest of the carrier gas is not stipulated[10] and that in principle it can vary (shorter at the beginning of the experiment and longer at the end). The only important factor is that the time during which the carrier gas flow is stopped should be significantly shorter than the half-life of the reactant. However, if one specifies the constancy of the duration of the arrests, then the numerical value of k can be found graphically with the aid of the relation:[29]

$$\lg P = \text{const} - \frac{kf}{2.303} \cdot t \quad . \qquad (8)$$

In order to calculate k for reaction (3) by Eqns.(6) and (7), the areas or heights of the "stop-peak" for any one, two, or all the compounds formed are measured. The last method is preferable if the chromatographic bands of the products are sufficiently separated.

For parallel reactions, for example, reaction (4), the ratio of the quantitative parameters of the peaks of compounds B and C after each arrest of the gas flow should be constant and the observed rate constant for the consumption of the reactant ($k_1 + k_2$) is calculated, as in the previous case, from the sum of the areas or heights of the "stop-peaks" B and C. The ratio of the areas of peaks B and C, adjusted to the same detection sensitivity and recorded after each arrest of the carrier gas, is equal to the ratio of the rate constants k_B/k_C.

Finally, when the consecutive reactions (5) take place, the ratio of the quantitative parameters of the "stop-peaks" of the products B and C does not remain constant. Furthermore, only the "stop-peaks" B will be symmetrical on the chromatograph. The superposition of the "tails" of the peak due to the reactant A and of the band of the intermediate compound B (formed continuously from A) hinders the differentiation of the band of the product C, which is formed during the arrest of the carrier gas flow (i.e. the "stop-peak" C). As a result, the accuracy of the determination of the rate constants for both the first stage (from the sum of the areas or heights of the "stop-peaks" of compounds B and C) and for the second stage (from the areas or heights of the "stop-peaks" C) is reduced. The accuracy of the determination of k_2 can be increased by measuring the rate constants for the second stage in independent experiments when the pure substance B is injected into the column-reactor.

In 1975–1978 Katsanos and co-workers developed a theory of the SFGC method on the basis of more complex models taking into account the non-ideality and non-equilibrium nature of slow diffusion and sorption processes in the column-reactor[13,14] and discussed the characteristic features of a first order chemical reaction in a dynamic regime under the conditions of ideal chromatography[15] taking into account the experimentally established fact that several (at least two) types of active centres exist on the surfaces of aluminosilicate catalysts.[41]

In the discussion of their model, the authors[13–15] rule out the spreading of the "plug" of the reactant or adsorbate vapour localised in the initial section of the space within the column-reactor and make the assumption that the isotherm of the distribution of the adsorbed species on all the centres is linear and that there is no longitudinal diffusion in the gas phase. For non-reaction systems, it is assumed that the establishment of interphase equilibrium in the column-reactor is inhibited solely by adsorption–desorption processes.[13,14] On the other hand, in describing the behaviour of the reaction system, the influence of sorption and diffusion processes is ruled out and the instantaneous distribution of reactants and products between the stationary and mobile phases is postulated.[15]

Having analysed the material balance established in the column-reactor throughout three artificially specified time intervals—before the first arrest, during the arrest, and after the flow has been restarted, Katsanos obtained a fairly cumbersome expression relating the area or height h of the "stop-peak", the duration of the arrest of the carrier gas flow t_s, and the rate of formation of the products R:[30–33]

$$R = \alpha \frac{h}{t_s} = \alpha m \left\{ \sum_{i=1}^{n} \frac{k_2^{(i)} k_1^{(i)} g^{(i)}}{\bar{k}_1 - k_2^{(i)}} \cdot \exp\left[-k_2^{(i)} t\right] - \left[\sum_{i=1}^{n} \frac{k_2^{(i)} k_1^{(i)} g^{(i)}}{\bar{k}_1 - k_2^{(i)}} \right] \cdot \exp\left(-\bar{k}_1 t\right) \right\} \quad . \qquad (9)$$

where α is a proportionality constant, m the mass of the injected reactant, and $g^{(i)}$ the fraction of reactant A absorbed on the ith active centre:

$$g^{(i)} = k_A^{(i)} \Big/ \left(1 + \sum_{i=1}^{n} k_A^{(i)} \right) \quad ,$$

$\bar{k}_1$ being the sum of the products $k_1^{(i)} g^{(i)}$:

$$\bar{k}_1 = \sum_{i=1}^{n} k_1^{(i)} g^{(i)} \quad .$$

For the simplest case of the irreversible first order reaction A → D on active centres of only one type without the formation of the intermediate B–S, i.e.

$$A + S \rightleftarrows A\text{—}S \xrightarrow{k} D\text{—}S \rightleftarrows D + S \quad ,$$

Eqn.(9) reduces to Eqns.(6) and (8). The applicability of Eqn.(9) has been confirmed in an experimental study by the SFGC method of the deamination of a number of aliphatic and alicyclic amines on the surface of Al_2O_3 [30,31] and silica gel[32] and also in a study of the kinetics of the dehydration of cyclopentanol and cyclohexanol on the surface of Al_2O_3 irradiated with neutrons in a nuclear reactor.[25]

In analysing the Katsanos model,[15] it is logical to assume that only part of the reactant is consumed in the formation of volatile products on the ith active centres of the adsorbent-catalyst; an appreciable fraction of the reactant can be sorbed irreversibly on active centres of another type with formation of involatile compounds, which should be manifested by a reduced conversion Q of the initial alkyl halide, alcohol, or amine. For example, in relation to the deamination of cyclohexylamine on two types of active centres on the Al_2O_3 surface, the following inequality holds for Q:

$$Q = (k_1^{(1)} g^{(1)} + k_1^{(2)} g^{(2)}) / \sum_{i=1}^{n} k_1^{(i)} g^{(i)} < 1 \, . \qquad (10)$$

The similarity of the numerical degrees of conversion of the initial cyclohexylamine into cyclohexene, calculated by Eqn.(10) and found by means of independent direct measurement, which has been discovered by Vattis et al.,[33] characterises the Katsanos model as fairly flexible. Nevertheless, we emphasise that the elimination of the influence of sorption and diffusion processes on the establishment of interphase equilibrium in the column-reactor during a chemical reaction, which has been adopted in this model,[15] is an artificial procedure which facilitates a formal description of the system within the limits of the conditions formulated. In fact the rate of accumulation of the product in the gas phase is an additive quantity determined by the set of the stages involving chemical reaction in the condensed phase and partition in the condensed phase–gas system. Only

when condition (1) holds, is it possible to obtain information about the chemical process from the results of headspace analysis. If, on the other hand, $k_r \gg k_e$, then the slope of the resulting relation will characterise the rate of mass exchange (the rate of extraction).

Under real experimental conditions, particularly in the study by the SFGC method of chemical reactions in solution in the stationary phase, situations frequently arise where $k_r \cong k_e$. The linear relation (8) is then transformed into a non-linear relation, because two exponential functions are superimposed, which is formally analogous to the case of two consecutive-parallel first order processes.

Thus the optimisation of the conditions under which headspace analysis is employed, including the conditions in a version of the SFGC method, for the investigation of the kinetics of the chemical process in the condensed phase should consist in seeking a regime ensuring the validity of inequality (1). In many instances, this problem can be readily solved when chemical reactions are carried out at fairly high temperatures on the surface of adsorbent-catalysts such as Al_2O_3, molecular sieves, and coarsely porous glass. At high temperatures, conditions governing the desorption of the volatile products formed do not limit the rate of their accumulation in the gas phase and the experimental relation (8) obtained makes it possible to find the constant for the rate of the chemical process on the surface of the adsorbent-catalyst.

3. Apparatus

The possibility of constructing gas connector schemes for SFGC on the basis of the experience gained in the development of combined gas-chromatographic analytical methods (interrupted gas chromatography) has already been mentioned above. The simplest versions of these schemes have been designed for use in a column-reactor linked directly to the detector (as a rule a flame-ionisation detector). The taps switching the gas flow are located outside the thermostatted zone directly ahead of the chromatograph evaporator.[10] In order to smooth the pressure drops in the system when the gas flow is switched off and then switched on, Katsanos and co-workers[13,29] used two consecutive stopcocks separated by a buffer reservoir (0.5–1.0 litre). We may note that this complication of the gas circuit of the apparatus is not essential, since the change in pressure in the column during the alternation of the arrest and flow of the gas has itself little influence both on the effectiveness and degree of separation. Thus, according to Walker and Wolf's data,[22] three consecutive arrests of the carrier gas flow lasting 0.5 min each caused a change in the effectiveness of the operation of the column and in the degree of separation of model hydrocarbon mixtures just as insignificant as a single arrest lasting 1.5 min.

The duration of the arrest of the carrier gas flow has a much greater influence on the spreading of the band in the column working in the SFGC regime. By carrying out comparative tests of three versions of the gas circuit, the authors[22] established that, when any one of the versions with both packed and capillary columns is used, brief interruption of the carrier gas flow (for 1–2 min) causes an insignificant alteration in the effectiveness and the degree of separation, which are, however, significantly reduced when the duration of the arrest is increased to several minutes. an analogous conclusion concerning the inverse proportionality between the duration of the arrest and the effectiveness of the column was reached in another study.[23]

A gas circuit similar to those employed in the studies mentioned[20,22,23,33] exhibits an appreciable inertia. Thus, according to data of Liebman et al.,[20] the lag during the period from the instant of turning the tap to the complete arrest of the carrier gas was 20 s, while according to other data[33] the difference between the specified and actual durations of the arrest reached 40 s. In the vast majority of studies carried out using SFGC, arrests of the carrier gas of identical duration (1–10 min) were specified and for this reason the corrections to the results of experiments associated with the inertia of the gas circuits were not made.

However, changes in the duration of the arrests of the carrier gas flow constitute a useful procedure when secondary processes accompanying the chemical reactions investigated appear, for example, autocatalysis by the water evolved or polymerisation of the olefins formed on dehydration of alcohols.[24] In those cases where the reactant arrest time is short, it is possible to formulate a series of experiments with single arrests of the carrier gas flow, which, however, are of different duration.[34,42,43] It has been observed[44] that, when very short arrests of the carrier gas flow are specified (down to 30 s, 5 s, or even 1.5 s), each resumption of the gas flow is accompanied by the recording of a negative signal.

In the majority of the reaction systems investigated by the SFGC methods, the expected composition of the product formed was fairly simple and there were no difficulties with their identification. In doubtful cases the procedure involving the trapping of the eluate fraction at the outlet from the column-reactor with its subsequent chromatography on analytical higher performance columns under the conditions of traditional eluent chromatography was resorted to. With the outlet from the reactor column connected directly to the detector, it is possible to obtain kinetic data for the variation of the overall composition of the products. The combined schemes, tested successfully in our laboratory,[45,46] are useful for the investigation of the kinetics of the formation of individual compounds. They include a column-reactor and an anlytical column located in autonomous thermostats of gas chromatographs (for example, of the Tsvet-100 series).

4. The Principal Results of Kinetic Studies by the SFGC Method

There exists a possibility, in principle, of using SFGC for the investigation of both heterogeneous catalytic processes and homogeneous reactions carried out in solution in the stationary and liquid phase (see, for example, Refs.11, 12, and 47). However, in practice the gas-adsorption version of chromatography is usually employed. Column-reactors 3–4 mm in diameter and 30–150 cm long are filled with adsorbents (Al_2O_3, modified alkali metal halides, silica gel, or coarsely porous glass) ensuring the stable retention of the reactant (alcohols, alkyl halides, amines, carbonyl compounds) and the rapid elution of the products of the dehydration, dehydrohalogenation, deamination, and hydrocracking reactions.

Experimental conditions under which the retention time of the reactant amounted to tens of minutes, hours, or even days while the retention time of the product was 1–5 min were selected for each type of reaction system, which made it possible to record tens and sometimes even hundreds of "stop-peaks" in a single analytical cycle for the duration of arrests of the carrier gas flow between 30 and 120 s.[11,24] The treatment of the experimental data consisted in the plotting of kinetic curves corresponding to an equation of type (8). Among the systems investigated, the simplest

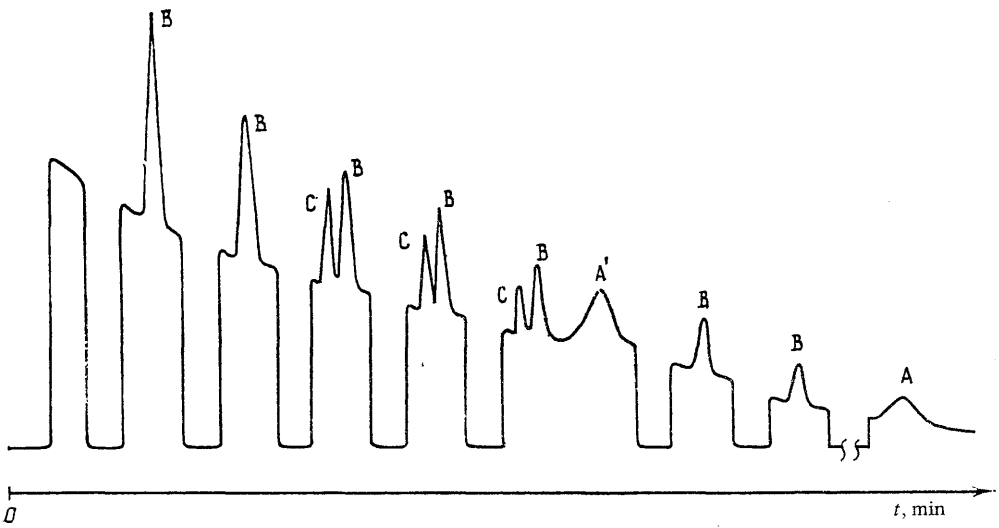
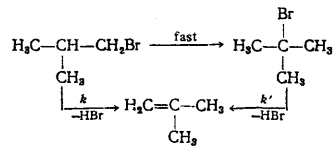


Figure 4. Chromatogram obtained in the study by the SFGC method of the dehydrobromination of isobutyl bromide on the surface of Al_2O_3 with 10 wt.% of LiCl:[27] A) isobutyl bromide; A') t-butyl bromide; B) isobutene (from isobutyl bromide); C) isobutene (from t-butyl bromide).

relations have been found for the dehydrohalogenation reaction. The reactants employed were cyclohexyl bromide, cyclohexyl chloride, cyclopentyl bromide[10] and also n-, s-, iso-, and t-butyl bromides.[33,34] The catalyst was γ-Al_2O_3 modified (10 wt.%) by the salts KCl, NaCl, CsCl, LiCl, KBr, NaBr, KI, and NaI. The reaction was carried out at different temperatures in the range from 50 °C to 150 °C. Depending on the specific reaction system and the experimental temperature, the numerical values of k varied from 20–30 s^{-1} to 30 min^{-1} and those of E_a from 50 to 130 kJ mol^{-1}. The simplicity and clarity of the experiment made it possible to recommend the investigation of the kinetics of the dehydrohalogenation of isobutyl bromide on an Al_2O_3 surface (with 10 wt.% of NaBr) by the SFGC method as a laboratory task in a University practical physical chemistry course.[29]§

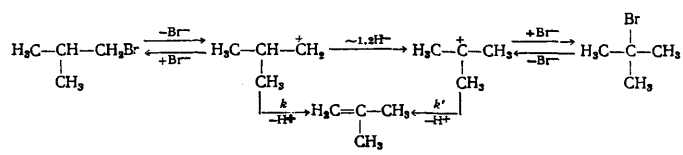
It has been possible to establish by the SFGC method[27] that the nature of the anion of the salt modifying agent has a major influence on the kinetics and mechanism of dehydrohalogenation. In particular, in experiments with isobutyl bromide and Al_2O_3, modified by alkali metal chlorides, after several single "stop-peaks" of the expected product (isobutene), two peaks began to be recorded on the chromatogram after each arrest of the carrier gas flow (Fig. 4). The study of the kinetics for each series of "stop-peaks" showed that two parallel reactions take place in the column-reactor, one of which is described by a first order kinetic equation and the other by a zero or first order equation, but with a very low rate constant. On the basis of the evidence that both peaks observed are due to isobutene, the authors[27] suggested that the initial isobutyl bromide undergoes on the surface of the catalyst, together with the elimination of HBr, isomerisation to t-butyl bromide which subsequently also loses HBr with formation of isobutene:



The double "stop-peaks" continued to be recorded until the elution from the column of the broad band due to t-butyl bromide, after which (until the initial isobutyl bromide emerged from the column) single "stop-peaks" were recorded on the chromatogram as at the beginning of the experiment.

When Al_2O_3 modified by potassium iodide (10 wt.%) was used, double "stop-peaks" were also observed,[28] but, in contrast to experiments with Al_2O_3 treated with an alkali metal chloride, these continued to be recorded even after the initial reactant had emerged from the column. Hence it was concluded that in the given case the initial isobutyl bromide is converted, via the intermediate formation of carbenium ions, into an alcohol which is dehydrated very slowly at the selected temperatures (~80–100 °C) and which is very strongly retained by the active centres of the adsorbent.

However, if the multistage mechanism of the dehydrohalogenation of isobutyl bromide by Al_2O_3 modified using metal chlorides is represented by



taking into account the scheme examined by Katsanos and co-workers,[27,28] the problem arises how rigorous is the attribution of the markedly different numerical values of k and k' to the different reactivities of isobutyl and t-butyl

§ A similar task has been successfully carried out for several years by the students of Course IV in the Gas Chromatographic Laboratory of the Faculty of Chemistry at Leningrad University.

bromides respectively. It is most probably caused by the differences between the stabilities and reactivities of the intermediate isobutyl and t-butyl cations.

We may note that the dehydrohalogenation reaction on the surfaces of the catalysts specified above are the only ones, among those investigated by the SFGC method, for which the carbenium ion mechanism has been adopted. For the related heterophase dehydration and deamination reactions, a concerted mechanism of the processes (*trans*-elimination) has been reliably demonstrated.

Another important result of the application of the SFGC method to the study of the elimination reactions is the conclusion that each can be carried out simultaneously on several (two–three) types of active centres on aluminosilicate catalysts. Attention was first drawn to this fact by Phillips et al.[12] The experimental kinetic curves for the dehydration of primary, secondary, and tertiary C_2–C_8 alcohols[24] on the surface of γ-Al_2O_3 with 10% of KCl were very close to the kinetic curve for the simultaneous decomposition of two radioactive isotopes. The conclusion that there are two types of active centres on the catalyst surface, drawn from the finding, is supported by the available information[41] concerning the presence of two types of aluminium ions in γ-Al_2O_3 (in tetrahedral and octahedral coordination states). Phillips and co-workers[24] do not rule out the presence on the surface of unmodified γ-Al_2O_3 and also of catalytic centres of a third type distinguished by an increased activity and suggested that the role of the modifying agent employed (KCl) consists in passivating these centres.

Subsequently the hypothesis of the possibility of the simultaneous dehydration on all three types of active centres was confirmed experimentally[25] and similar relations were observed also in the study of the deamination reaction.[32]

The observation of identical kinetic relations for the deamination and dehydration reactions on the surfaces of aluminosilicate catalysts is noteworthy. The experimental kinetic curves for both processes using different Al_2O_3, porous glass, and silica gel specimens as catalysts at relatively low temperatures pass through a maximum and then fall steeply. An increase of temperature leads to the disappearance of the ascending section of the curve and to the approach of the remaining descending branch to the form of a simple exponential relation.

Mathematical analysis of the kinetic curves obtained showed that they can be adequately described by the following empirical equations:

$$R = a_1 \exp(-b_1 t) + a_2 \exp(-b_2 t) + a_3 \exp(-b_3 t)\,, \qquad (11)$$

$$R = \sum_{i=1}^{3} [a_i \exp(-b_i t)] - a_4 \exp(-b_4 t)\,. \qquad (12)$$

where R is the rate of formation of the product and a_i and b_i are positive constants which depend on the catalyst, the reaction investigated, and temperature. Eqn.(11) is valid for processes which proceed with participation of two types of active centres on the catalyst surface (deamination of amines on the Al_2O_3 surface[30,31]), while Eqn.(12) characterises reactions occurring on active centres of three types (deamination of amines on the surfaces of coarsely porous glass and silica gel,[32] dehydration of alcohols on the Al_2O_3 surface irradiated with neutrons[25]).

Both empirical equations, (11) and (12), agree fully with Eqn.(9) proposed previously.[15] The rate constants k_1, $k_2^{(1)}$, $k_2^{(2)}$, and $k_3^{(3)}$ were found from graphical relations of type (13) or using non-linear regression analysis with the aid of a computer.[25]

Since the absolute numerical values of k (like the absolute retention parameters in gas chromatography) are influenced by various experimental factors (the characteristic features of the preparation and conditioning of a particular column-reactor, its size, etc.), it was suggested as early as 1970 [24] that the relative reactivities of the substrates be estimated by the method of competing reactions, injecting simultaneously into the column-reactor a mixture of two alcohols—the test alcohol and one selected as the standard. Unfortunately, this procedure was not developed in the subsequent practical employment of SFGC. Furthermore, the error in the measurement of the absolute values of k, obtained in experiments on different apparatus and columns, can reach 400%, while the reproducibility of the relative quantity k_1/k_2 is to within 10–15%.[24]

As a consequence of the very strong sorption of alcohols on the Al_2O_3 surface, the reactants hardly move in the column-reactor along the catalyst bed, which makes it possible to carry out a very large number (tens and hundreds) of measurements in each individual experiment in the study of dehydration kinetics by the SFGC method. Throughout such a long cycle, it is possible to carry out a stepwise variation of the temperature of the column-reactor and to obtain data necessary for the determination of the activation energy E_a without resorting to the additional injection of reactants. Phillips and co-workers[24] note correctly that the inadequate accuracy of the measurement of the numerical values of E_a (±1.5 kcal mol^{-1}) precludes any reliable conclusions about the character of the variation of E_a as a function of structure within the limits of an isotypical series (for example, in the series of normal primary or normal secondary alcohols), which, in their view, would have been possible if the error could be reduced to ±0.5 kcal mol^{-1}. Nevertheless, their results[24] reveal an appreciable difference between the activation energies for the dehydration of primary alcohols, on the one hand, and secondary and tertiary alcohols, on the other. One should note the proportional variation of the numerical values of E_a and $\ln A$ (the pre-exponential factor in the Arrhenius equation), which indicates the operation of the so-called compensation effect.

Most of the results obtained in the above study[24] refer to the kientics of the dehydration reaction on "slow" active centres of the modified Al_2O_3. Katsanos and co-workers[25,32] determined and compared the numerical values of E_a and $\ln A$ for each type of "slow" and "fast" active centres on the catalyst employed in the deamination and dehydration reactions. Having confirmed the operation of the compensation effect in all cases, they concluded that each type combines a group of centres characterised by the same values of $\ln A$ but different E_a.[25]

The application of the SFGC method to the study of the kinetics of the hydrocracking of hydrocarbons on the Ni–SiO_2 surface at temperatures in the range 160–220 °C established unusually high values of E_a (300–550 kJ mol^{-1}); the values of E_a depend so strongly on the structural features of the compounds of a particular homologous series (n-alkanes, isoalkanes, and cycloalkanes) that this can be used in group analysis.[34]

Subsequently the behaviour of aliphatic aldehydes[35] and ketones[36] on the Ni–SiO_2 surface at temperatures in the range 130–200 °C was investigated. It was established that, under the given conditions, the reactions involving the hydrogenolysis of aldehydes and the dehydrogenation of ketones respectively predominate. The hydrogenation of aldehydes and the hydrocracking of the resulting alkanes are concomitant processes whose role increases with increase of temperature. At a temperature of 300–350 °C, the only reaction products are methane and water, which agrees with

the data obtained in our laboratory¶ using a nickel–aluminium catalyst prepared in accordance with the recommendations of Grumbuller et al.[48]

Scott et al.[35] suggest that the hydrogenolysis of aldehydes is limited by two kinetically independent consecutive stages: the RCH_2CHO molecules adsorbed initially on the surface are slowly cleaved to the alkane RCH_3, which is desorbed to the gas phase, and the CHO fragment, which remains in the adsorbed state and is in its turn slowly reduced to CH_4.

Ketones are hydrogenated in one stage and the similarity of the kinetics of the reduction of the intermediate HCO in the case of aldehydes and adsorbed molecules of the ketones RR'CO, established by Abdulah and Sulaiman,[36] is an important experimental fact.

5. Application of Discrete Gas Extraction in a Single Chromatographic System to the Solution of Analytical Problems

As already mentioned above, apart from the rigorously stoichiometric reaction in the chromatographic column-reactor in accordance with schemes (2)–(5), some of the reactant molecules can be sorbed irreversibly on the surface of the sorbent-catalyst with formation of involatile compounds and can also be converted into side products (mainly relatively involatile polymers); sometimes, and this is especially characteristic of reactions in solution in the stationary liquid phase, the "breakthrough" of the reactant through the reactor is observed. The knowledge of the amount (fraction) of the reactant which has reacted is important for the estimation of the degree of conversion via the relevant pathway.

In the quantitative reaction of the reactant via pathways (2)–(5), the determination of its initial content in samples analysed having a complex composition is an important task for analytical reaction gas chromatography. The method of determining the initial concentration of the reacting compound, based on the knowledge of the kinetic parameters of the reaction, was first proposed in a study[49] where a pulsed chromatographic method was used to measure the reaction rate constant k and the current concentration of the reactant c_i at time t_i, this being followed by the calculation of the initial concentration c_0 by the familiar equation

$$k=\frac{1}{t_i}\ln\frac{c_0}{c_i} .$$

The method was tested in relation to the interaction of butadiene with maleic anhydride. The chromatographic reactor was placed beyond the separating column. The time of contact between the reactants was determined by carrying out experiments at different carrier gas flow rates on the assumption that the contact time is inversely proportional to the gas flow rate. In order to determine c_i, a non-reacting compound (internal standard) was introduced into the initial specimen. The disadvantages of this method are the long time required, the necessity for several analytical cycles with the reactor disconnected or connected at different carrier gas flow rates, and the difficulties in the selection of a suitable standard compound.

A chromatokinetic method has been developed recently[46] for the determination of the initial content of the reactant, based on the discrete extraction of volatile products from the reaction zone of the chromatographic reactor by the carrier gas. The combination in a single analytical cycle of the stages involving the measurement of the reaction rate constant k and the determination of the amount of products m_i formed during a fixed period t_i must be regarded as advantages of this method. The constant k was measured by the SFGC method using Eqns.(6) and (8). The amount of products formed during a specified time was found by the method involving the absolute calibration of the chromatograph. The method was tested successfully in relation to the dehydration of cyclohexanol and also s- and t-butyl alcohols to the corresponding olefins in a chromatographic column-reactor on the surface of a diatomaceous carrier coated with a layer of phosphoric acid. The initial content of the alcohol m_0 was found from a rearranged first order kinetic equation:

$$m_0=m_i/(1-e^{-kt}) . \qquad (13)$$

The relative error of the determination did not exceed 10% on average.

Equations analogous to Eqn.(13) can be used also to determine the content of the substance which has reacted in the quantitative headspace analysis of reaction systems in autonomous reactors outside the chromatograph.[50,51]

A discrete gas extraction procedure, analogous to the SFGC method in its experimental aspect, has been used[52,53] to investigate the dynamics of desorption and to determine the overall content of volatile impurities in polymeric materials. The finely dispersed polymeric material was placed in a glass insert in one of two parallel evaporators of the chromatograph connected to the analytical column via a T-junction. The carrier gas was passed periodically either through the empty evaporator or through the chamber with the specimen, all the volatile products evolved into the gas phase during the preceding period being directed to the column. Since the rate at which the volatile impurities are transferred from the solid polymer to the gas phase is proportional to their concentration and formally obeys a first order kinetic equation, the overall content of the volatile component can be found, according to Kolb and Pospisil,[52,53] from the results of only the first two extractions.

The problem of determining the overall content of the volatile impurities diffusing from polymeric materials has been solved in a more general form by Ioffe and co-workers, who suggested that the results of discrete gas extraction in open systems be subjected to a treatment involving the measurement and subsequent allowance for the so-called buffer coefficient B, which characterises the fraction of the non-extracted substance and is equal to the ratio of the areas S or the heights h of the peaks on the chromatograms of the vapour phase obtained in two successive extractions:[54]

$$B=\frac{m_{n+1}}{m_n}=\frac{c_{G(n+1)}}{c_{G(n)}}=\frac{S_{n+1}}{S_n}=\frac{h_{n+1}}{h_n} , \qquad (14)$$

where m is the mass of the extracted substance, c_G the concentration of the extracted substance in the gas phase, and n the number of the extraction.

In the general case, the quantity B can change during extraction, but for analytical purposes systems characterised by constant buffer coefficients are the most suitable. For B = const, the amounts of substance contained in the extract form a geometrical progression with B as the denominator and the total amount of substance extracted M_0 can therefore be determined without carrying out an exhaustive extraction:

$$M_0=\sum_{n=1}^{\infty}m_n=\frac{m_1}{1-B} \qquad (15)$$

The number of successive extractions necessary for the accurate estimation of the buffer coefficient by Eqn.(14) should be as small as possible owing to the risk of the distorting influence of the "memory" of the apparatus and the

¶ See B.V.Stolyarov and E.E.Galev "Tezisy Dokladov IX Vsesoyuznoi Konferentsii po Gazovoi Khromatografii" (Abstracts of Reports at the IXth All-Union Conference on Gas Chromatography), Kuibyshev, 1987 (in the press).

impairment of the phase equilibration conditions after many repetitions of the cycles involving flushing of the chamber with the specimen by the extractant gas.[55]

The authors of all the published studies on the practical employment of SFGC methods have failed to note the interfering influence of the above factors, although, according to the data of Ioffe et al.,[55] one cannot rule out the undesirable manifestation of the "memory" of the chromatographic system, especially after a large number of cycles involving the arrest and movement of the carrier gas. As a result of this, it is necessary to ensure fairly high concentrations of the compounds extracted in the gas phase and to confine oneself to the minimum necessary number of extractions for the solution of the given specific problem.

For a number of reaction systems resistant to high temperatures and characterised by low partition coefficients of the products formed, even a single arrest of the gas flow, sometimes combined with a sharp increase of the temperature of the column-reactor during the arrest, can ensure the quantitative conversion of A into B and the exhaustive extraction of the products from the condensed phase. The effective concentration of the impurities during their desorption from the surface of the sorbent in the absence of chemical reaction can be ensured in exactly the same way.[56]

The first example of the employment of the SFGC method for strictly analytical and not kinetic purposes has been the concentration, proposed by Phillips and co-workers,[11,12] of aliphatic alcohols as microimpurities from air or organic solvents on Al_2O_3 with their subsequent dehydration involving a single arrest of the flow (for 7 min) and with the simultaneous increase of temperature from 150° to 450 °C. The subsequent cooling of the column-reactor to the initial temperature and the restart of the carrier gas flow lead to the recording on the chromatogram of distinct olefin peaks, which are readily susceptible to integration.

A second example of the successful employment of a single arrest of the gas flow for analytical purposes is provided by a study carried out recently in our laboratory.† It was shown that a single arrest of the gas flow lasting 1 min is sufficient for the exhaustive hydrogenolysis of organic compounds of different classes on the surface of a nickel-aluminium catalyst in a hydrogen atomsphere at 350–400 °C. The new simple method for the determination of the total organic carbon in water and in aqueous solutions, developed in the above study, is based on the exhaustive conversion of carbon-containing compounds into methane, which is extracted in a single step by the mobile phase (hydrogen) from the surface of the catalyst. The relative error did not exceed 10% and the threshold sensitivity was 5 mg C litre^{-1}.

The disadvantages and limitations of headspace analysis in the SFGC version in the solution of both kinetic and analytical problems should be noted. In the first place, the method is applicable only to the investigation of processes whose kinetics are described by first order equations. The second disadvantage is the reduction of the accuracy of the measurement under the influence of diffusion of the extracted substance in the mobile phase during the arrest of its movement, which is aggrevated by the inertia of the gas circuit usually employed. An important limitation of the application of the SFGC method to the study of reaction systems is the necessity to ensure a greater retention of the reactant by the stationary phase compared with the retention of the products.

†See B.V.Stolyarov and E.E.Galev, "Khimiya i Tekhnologiya Vody" (The Chemistry and Technology of Water) (in the press).

III. REVERSED FLOW GAS CHROMATOGRAPH

1. Principles, Apparatus, and Applications of RFGC

The gas chromatographic method with periodic change (reversal) of the carrier gas glow (RFGC), which is related to the SFGC method but is free from its main limitations, was proposed in 1980 by Katsanos.[57,58] The initial versions of the RFGC method were designed for the measurement of the kinetic parameters of chemical reactions on the surface of the adsorbent-catalyst in chromatographic column-reactors (a simple single stage first order reaction processes including two consecutive stages).[57,58] However, subsequently the applications of the method were greatly extended and RFGC was used to investigate the dynamics of adsorption and desorption, to measure the diffusion coefficients of volatile compounds in different gases, and to determine the activity coefficients of components of solutions.[59] The relative molar responses of the thermal conductivity detector and hence the molecular diameters and the critical volumes of different gases, the Lennard-Jones parameters, and the coefficients of the mass transfer of n-alkanes from the surface of Porapak P to a mobile gas phase (see below) have been measured recently by the RFGC method.

The fundamental possibilities of the RFGC method are illustrated in Fig.5. In contrast to SFGC, in the RFGC method the products concentrated in a limited volume of the mobile phase are sampled at fixed times by the repeated alteration of the direction of flow of the mobile phase and not by means of periodic arrests of the carrier gas flow. We shall consider one of the possible versions of the apparatus for the method. The reactor has the form of a T-piece, two arms of which (l and l') are alternately flushed with the carrier gas in opposite directions (F and R) by rotating the shell of the switching six-way tap ST (Figs.5*a* and 5*b*). The third arm L is at right angles to the first two and is used either for the evaporation of the reactant or for its pulsed injection directly into the adsorbent or catalyst bed. The catalyst or adsorbent are placed in sections l and l' in the stream of carrier gas. The gas circuit includes also the separating analytical column AC, which can be replaced by a permanent constriction. If after the injection of the reactant the position of the shell of the switching tap ST is altered periodically (at time intervals exceeding the retention time t_{RB} of the products in sections l and l' respectively), then one obtains a series of the so called F and R peaks associated with the movement of the gas in the forward (F) and reverse (R) directions. Each reversal of the gas flow then leads to the effective compression and symmetrisation of the band of the product continuously extracted from the reaction zone by the moving gas (Fig.5*c*).

The effectiveness of the concentration of the product in the gas plug directed to the detector can be increased by employing double flow reversal, which is entirely analogous to the replacement of single gas extraction by two consecutive extractions using the same volume of extractant gas. Having reversed at time $t_1 > t_{RB}$ the initial direction of the gas flow (F) to give the opposite flow (R) and without waiting for the recording of the peak of the extracted substance on the chromatogram, the tap is turned again, after a time interval Δt (several seconds) shorter than the retention time of the product t_{RB} in the l and l' sections of the reactor, returning the flow to the direction F. After recording the peaks of the products, the cycle is repeated, keeping constant the selected flow reversal time interval Δt. The form of the resulting chromatogram is illustrated in Fig.5*d*. If it is necessary to increase the extraction time during a

single cycle, the number of passes of the carrier gas through the l and l' reactor sections in the forward and reverse directions can be increased an even number of times.

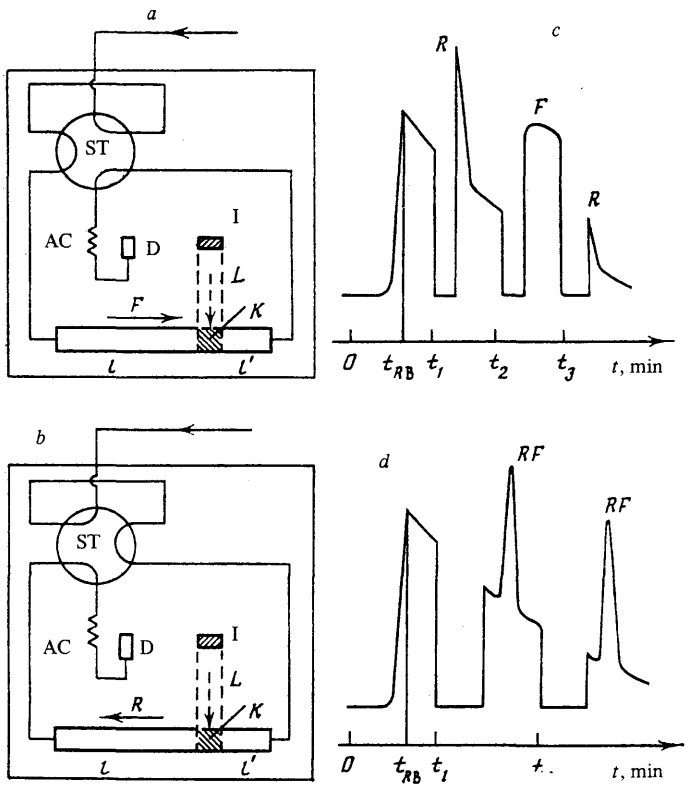


Figure 5. Schematic illustration of the apparatus for RFGC and specimen chromatograms (for explanation, see text).

For reaction systems with small and similar partition coefficients of the reactants and products between stationary and mobile phases and also in those cases where two gaseous reactants are used, none of which is the carrier gas, the catalyst bed is placed in the reactor branch L through which the carrier gas is not passed. The reactants (one or two) are introduced through the sample injection unit I; the end-face of the section is sometimes connected to a U-shaped tube containing 1–0.5 ml of the liquid reactant; a constant flow of the reactant vapour to the catalyst surface is thereby ensured.[59]

These procedures make it possible to investigate the kinetics of slow chemical reactions not only with respect to the reaction product but also with respect to the reactants provided that both are eluted from the catalyst bed together and are separated either in the sections l and l' of the reactor or in the analytical chromatographic column placed before the detector. In those cases where the volatile products and reactants pass from the reaction zone to the bulk of the carrier gas (i.e. to the reactor arms l and l') as a result of diffusional flow, this must be taken into account in interpreting the experimental results. The diffusion of the reactants and products in the carrier gas can be investigated in independent experiments using reactors unfilled with the sorbent.[60–63]

2. Determination of the Rate Constants for Chemical Reactions and Diffusion and Adsorption Coefficients

The analytical mathematical expressions permitting the determination of the equilibrium constant of a slow chemical or physical process from RFGC data depend on the process model adopted and on the chromatographic characteristics of the reactant and product.

We shall consider, for example, one of the simplest cases referring to first order reactions A → B, where the reactant A is rapidly adsorbed on the catalyst surface containing only isotypical active centres S. The compound A–S is then formed and is slowly converted into the adsorbed product B–S and the latter reaches equilibrium with the product B in the gas phase:

$$A + B \underset{K_A}{\overset{\text{fast}}{\rightleftharpoons}} A-S \xrightarrow{k} B-S \overset{\text{fast}}{\underset{K_B}{\rightleftharpoons}} B + S,$$

where K_A and K_B are the partition coefficients of the reactant A and the product B respectively, with $K_A \gg 1$, and k is the reaction rate constant.

The kinetic experiment provides for the measurement of the amount of product accumulated in the gas phase volume of the reactor column during the time intervals between the successive changes in the direction of flow of the carrier gas, i.e. during the first R interval—from the instant t_1 (when the F direction changes to R) up to the instant t_2 (when the initial direction of the carrier gas flow is restored); the subsequent F interval extends from the instant t_2 to the corresponding instant t_3 when the direction of flow is switched (Fig. 5c), etc. These time intervals should be shorter than the retention time of the reactant when the carrier gas moves in the forward and reverse directions.

Analysis of the material balance equation established for the system during the time intervals specified above makes it possible to relate the quantitative parameters of the F and R peaks (their areas or heights—P_F and P_R respectively) to the mass of the reactant m, the fraction of its molecules sorbed on the active surface centres f, the retention parameters of the product when it is eluted in the forward direction (t_R^F for the F peaks) or the reverse direction (t_R^R for the R peaks), and the total time (t_{tot}) elapsed from the instant of injection of the reactant to the subsequent reversal of the carrier gas flow:

$$P_R = mf\,[\exp(kt_R^F) - 1]\exp(-kt_{tot}); \qquad (16)$$

$$P_F = mf\,[\exp(kt_R^R) - 1]\exp(-kt_{tot}). \qquad (17)$$

In the case of a single stage first order chemical reaction of the type A → B under consideration, the graphical dependence of $\ln P_R$ and $\ln P_F$ on the time t_{tot} is represented by a straight line, from the slope of which the rate constant k can be found.

The physical significance of Eqns. (16) and (17) becomes more understandable when they are rewritten in the following form:

$$P_R = mf\exp[-k(t_{общ} - t_R^F)] - mf\cdot\exp(-kt_{tot}); \qquad (18)$$

$$P_F = mf\exp[-k(t_{общ} - t_R^R)] - mf\cdot\exp(-kt_{tot}). \qquad (19)$$

It is seen from Eqns. (18) and (19) that the peak areas are directly proportional to the retention times of the product with the carrier gas moving in the forward and reverse directions, so that all the experimental points should lie on a single straight line for rigorously identical lengths of the sections

of the column-reactor ($l = l'$, Figs. 5*a* and 5*b*). When the lengths of the column-reactor sections are unequal, for example for $l' < l$, the R peaks should be smaller than the F peaks (and conversely). In this case the identical slopes of straight lines (18) and (19) can be regarded as proof of the absence of secondary effects (for example, the autocatalysis by the water evolved or the polymerisation of the olefins formed on dehydration of the alcohols) in the course of the conversion of the reactant A into the product B for different contact times with the active catalyst centres.

The non-linear character of the dependences of $\ln P_R$ and $\ln P_F$ on the time t_{tot} indicates a more complex process mechanism and the presence of not one but several rate-limiting stages. Some of them can be purely physical, for example, they can be determined by the slow diffusion of the reactant from the gas phase to the catalyst surface or the slow mass exchange of the products between the mobile and stationary phases.

In particular, in the study by the RFGC method of the deamination of aminocyclohexane on the γ-Al_2O_3 surface at 247 °C,[69] kinetic relations typical for two first order consecutive reactions were obtained. The application of RFGC to the study of processes with several consecutive-parallel first order stages has been examined by Katsanos and Kotinopoulos,[64] while Katsanos et al.[65] considered its application to the study of single stage reactions with a fractional order.

The case where the product and reactant are hardly sorbed on the catalyst surface and are eluted simultaneously is of special interest. This version has been considered in relation to the oxidation of CO to CO_2 by oxygen,[66] the hydrogenation of propene,[65] and the hydrodesulphurisation of thiophen to butane and butenes.[67] In solving problems of this kind, account must be taken of the complications associated with the diffusional flow of the reactant onto the catalyst surface. The concentration of the products or reactants at a fixed time is obtained by measuring the height of the corresponding chromatographic peaks. The concentration of the reactants depend on time, the diffusion coefficients, the catalyst mass, the volume flow rate of the carrier gas, and the rate of the chemical reaction. The concentration of the products depends in its turn on the rate of the chemical reaction, the mass of the catalyst, and the volume flow rate of the carrier gas. The expression for the reaction rate constant is as follows:[67]

$$k = \frac{v}{m_c} \ln \frac{1}{(1-x)} ,$$

where v is the volume flow rate of the carrier gas, m_c the mass of the catalyst, and x the fraction of the reactant converted into the product.

In particular, in the study of the reaction kinetics on the basis of the consumption of the reactant, we obtain the expression[67]

$$x = \frac{h_0^{(r)} - h^{(r)}}{h_0^{(r)}} ,$$

where $h_0^{(r)}$ is the height of the detector signal corresponding to the initial reactant concentration and $h^{(r)}$ the height of the detector signal corresponding to the concentration of the reactant which has passed through the catalyst bed.

3. The Principal Results of the Employment of the RFGC Method in Kinetic Studies

The reaction systems investigated by the RFGC method are of two types:

$$A \xrightarrow{\text{catalyst}} D + E + \ldots ,$$

where A is the reactant strongly sorbed on the catalyst surface and undergoing slow decomposition and D and E are the volatile reactant decomposition products detected, and

$$A + Z \xrightarrow{\text{catalyst}} D + E + \ldots ,$$

where A and Z are reactants weakly sorbed on the catalyst surface (one of them may be the carrier gas—for example, hydrogen) and D and E are the volatile reaction products detected.

The first group includes the dehydration of lower alcohols (propyl, isopropyl, and n-butyl[68]), the deamination of propyl-, isopropyl- and cyclohexyl-amines[68,69] on the surfaces of zeolite 13X and Al_2O_3, and also the catalytic cracking of cumene on the LaY and HY zeolites.[64] The second group combines the reactions involving the oxidation of CO by gaseous oxygen under the influence of Co_3O_4 deposited on Al_2O_3 modified with Ca^{2+},[66] the hydrogenation of propene on platinum (5% Pt on Al_2O_3),[65] and the hydrodesulphurisation of thiophen on the surfaces of catalysts with a complex composition, containing MoO_3 and Co_3O_4.[67]

The kinetics of the dehydration of alcohols have been investigated in the temperature range 179–385 °C, the first order of the reaction has been confirmed, and evidence for the absence of secondary processes on the catalyst surface has been presented.[68] The observed rate constants and activation energies agree fairly well with the literature data obtained by other methods, in particular by the SFGC method, using catalysts of similar composition.[24] Unfortunately, Katsanos and co-workers,[68] who previously employed actively the SFGC method for purposes including also the study of the kinetics of the dehydration of alcohols,[25] did not carry out direct experiments with the same reactants and catalysts for the purpose of the comparative assessment of the values of k and E_a obtained by the SFGC and RFGC methods. The only example of such a comparsion refers to the deamination reaction on Al_2O_3, the study of which by the SFGC and RFGC methods yielded results in satisfactory agreement.[33]

The reversal of the carrier gas flow made it possible to establish that the deamination reactions of propyl-, isopropyl-, and cyclohexyl-amines on the zeolite 13X in the temperature range 297–424 °C are described by a first order equation with a single rate-limiting stage, while on the active centres of γ-Al_2O_3 cyclohexylamine is deaminated via a mechanism including two consecutive first order reactions. With the aid of RFGC, it is possible to determine readily the numerical values of the rate constants for the rate-limiting stages, but the method does not enable one to discover to which particular stage each of the constants obtained refers.[69]

The most complex process investigated by the RFGC method is the cracking of cumene, catalysed by zeolites at 252 to 338 °C, to the study of the kinetics of which an extensive literature has been devoted.[64] It has been established that, depending on the nature of the catalyst, the kinetic process mechanism proposed previously[70] includes either one or two rate-limiting stages, but, as in the simpler cases considered before, the RFGC method does not enable one to find out which particular stages are rate-limiting.

It is noteworthy that compression of the product bands in the free volume of the reactor as a result of the reversal of the carrier gas flow leads to the loss of information about

the number of types of active centres on the catalyst surface. In the interpretation of the RFGC data, this question is not even posed, while in studies on the theory[15] and the practical application[10,24,25,32] of the SFGC method much attention is devoted to precisely the determination of the role of the so-called "fast" and "slow" active centres of the catalyst.

On the other hand, the principle of the reversal of the carrier gas flow underlying RFGC made it possible to extend the application of the gas-chromatographic headspace analysis in kinetic studies and to include among such applications the study of reaction systems with reactants which are not retained on the adsorbent-catalyst bed, including systems with two gaseous reactants neither of which is the carrier gas. The study[66] of the kinetics of the oxidation of CO by molecular oxygen, catalysed by Co_3O_4 deposited on a zeolitic carrier modified with Ca^{2+}, is instructive in this respect.[66] The above study demonstrated experimentally the first order of the reaction with respect to CO, the reaction rate constants were determined in the temperature range 168–279 °C, and it was established that, with increase of the content of calcium ions in the catalyst (from ~0.4 to ~2.5 mmol g^{-1}), the activation energy for the oxidation of CO diminishes in proportion (from ~33 to ~14 kJ mol^{-1}) and then increases linearly (to ~44 kJ mol^{-1}). These observations clearly illustrate the possibilities in the employment of SFGC for the estimation of the comparative activities of catalysts of different composition.

The possibilities of the RFGC method are by no means restricted to the study of the kinetics of only first order processes. Thus a detailed investigation has been made[65] of the kinetics of the hydrogenation of propene by hydrogen and a catalyst comprising 5% of platinum on Al_2O_3 (carrier gas–nitrogen) at 136–166 °C. The fractional reaction order with respect to hydrogen, varying from 1.6 to 2.5 depending on the surface coverage of the catalyst by hydrogen, has been established by treating the experimental data using numerical methods.

Among the chemical reactions investigated by the RFGC method, the hydrodesulphurisation of thiophen to butane and butenes in a stream of hydrogen on aluminosilicate catalysts is of special interest.[67]

It is significant that the kinetic parameters of the diffusion and adsorption processes uncomplicated by accompanying chemical reactions can be investigated also in independent experiments using the RFGC method. Thus measurements have been made[60–62] of the diffusion coefficients in different carrier gases (H_2, He, N_2) for a series of lower gaseous alkanes and alkenes (both individual compounds and binary mixtures) and the temperature dependence of the diffusion coefficients has been found. A study has been devoted[63] to the application of the RFGC method to the measurement of the rate of evaporation of liquid C_5–C_8 n-alkanes and C_1–C_5 alcohols at 20–101 °C and to the simultaneous measurement of the diffusion coefficients of their vapours in helium. The adsorption of lower alkanes and alkenes on Al_2O_3 has been studied by Katsanos and co-workers,[71] while an investigation of the desorption of organic solvents (pentane, hexane, and acetone, and acetic acid) from the Al_2O_3 surface was described by the same workers in another communication.[72]

Slight changes in the experimental methods described above made it possible to determine, simultaneously with the measurement of the diffusion coefficients of air, oxygen, nitrogen, argon, CO_2 and lower gaseous alkanes and alkenes in the carrier gas (helium), also the relative molar sensitivities of the thermal conductivity detector with respect to the above substances and to characterise the critical volumes, molecular diameters,[73] and Lennar-Jones parameters.[74] The activity coefficients of methanol, ethanol, and 1-propanol in aqueous solutions at different concentrations have been measured by the SFGC method at 50°, 60°, and 65 °C respectively.[75] The application of RFGC to the determination of the mass transfer coefficients and also of the turbulent and longitudinal diffusion coefficients of hexane, heptane, and octane on columns filled with Porapak P (carrier gas–helium) has been discussed.[76]

We may note that the combination of the principles of RFGC and the circulation method proposed by Berezkin and Shiryaeva[77] may prove useful for the kinetic study of very rapid processes.

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The data described in this review permit the conclusion that stopped flow and reversed flow gas chromatographic methods possess great possibilities, which have not yet been ultimately elucidated, for the investigation of the kinetics of chemical reactions and slow physical processes (diffusion, evaporation, sorption) in chromatographic column-reactors and are also promising for the solution of certain important analytical problems (determination of volatile impurities and of the overall content of chemical elements in different objects, determination of the initial content of the reactant).

For the further development and effective use of the SFGC and RFGC methods, it is essential to optimise them using the mathematical experimental design procedures. However, one can already say that both methods considered constitute a convenient instrument in the rapidly developing gas-chromatographic headspace analysis of reaction systems.[46,50,51]

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