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Abstract

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CHEMICAL REACTIONS IN A CHROMATOGRAPHIC REGIME

Chemical reactions carried out in a flow in contact with the surface of a condensed phase are at first always accompanied by at least partial separation of the components of the reaction mixture. This separation may occur in chemical reactions: 1) of gases and liquids catalyzed by solids; 2) of gases and liquids reacting homogeneously in the presence of solids capable of absorbing, to different degrees, the components of the reaction mixture; 3) of gases and vapors reacting homogeneously over the surfaces of liquids that dissolve individual components; 4) in topochemical reactions of solids in a flow, etc.

Under the conditions of an ordinary prolonged dynamic experiment, chromatographic effects are initial distortions which disappear after some time. Thereafter, in each section perpendicular to the direction of the flow, a constant ratio of the concentrations of the starting substances and products is established, corresponding to the steady course of the process under dynamic conditions.

Using special techniques of analytical chromatography, it is possible to create conditions under which separation occurs during a large part of the time of passage of the substances through the reaction apparatus. In this case, as will be seen from what follows, separation can have a substantial influence on the character of chemical processes, and therefore one may speak of special chromatographic regimes for carrying out chemical reactions.

In analyzing chemical processes in a chromatographic regime, we shall restrict ourselves to the case in which the rate of the chemical process is considerably smaller than the rate of mass exchange between phases. As a basis we shall take the simplest and most illustrative case of the reaction of a portion of substance, introduced in the form of a pulse into a stream of carrier gas entering the reactor. Such a method of carrying out a reaction has recently begun to acquire importance in the study of catalytic processes ([1,2]).

Let us consider the reaction

$$\nu_A A \rightarrow \nu_B B + \nu_C C.$$

Let us introduce into the stream a mixture $A + B + C$. We shall assume that the distribution coefficients b_i of the substances between the two phases are unequal.

If $b_A < b_B < b_C$, then at some distance from the inlet into the reactor three bands should form (Fig. 1a). In the absence of reaction these bands will move along the reactor, gradually separating. In the case of reaction, substances B and C are continuously generated in zone A; they will form characteristic tails behind the band of the reacting substance A (Fig. 1b). If $b_A > b_B > b_C$, the reacting substance A will send B and C forward (Fig. 1c). The case $b_B < b_A < b_C$ is shown in Fig. 1d.

Thus, despite the presence of all components in the initial mixture and the generation of products in the course of the reaction, in the chromatographic regime a more or less complete separation of the products from the initial reacting substance will be observed. It should be noted that the picture described must be

qualitatively the same for homogeneous and heterogeneous reactions. The formation of zones of the individual components of the initial reaction and of any foreign substances present in the system leads to a number of specific features of the chromatographic regime. Let us consider some of them:

1. Reversible reactions of the type

$$A \rightleftarrows B + C + \dots + N$$

When $b_i \neq b_N$ for at least one pair of products, the reaction proceeds only from left to right. It is interesting to note that only when $b_B = b_C = \dots b_N$ can the reaction in the chromatographic regime proceed in both directions and retain its reversibility. The features of this case are already evident in the simplest example of the isomerization reaction

$$A \rightleftarrows B.$$

When substance A is introduced into the reactor (with $b_A < b_B$), the A band will be accompanied by a "tail" of B, from which A will in turn be formed. Thus, the rate of the forward reaction can be determined from the amount of unreacted A.

With simultaneous introduction of A and B, the picture will not change substantially, and in the A band the practically irreversible forward reaction will proceed, while in the B band the reverse reaction will proceed.

2. Reaction involving 2 or more starting substances

$$\nu_A A + \nu_B B + \dots \to \nu_K K + \nu_M M + \dots$$

Figure 1. Output curves in conducting a chemical reaction in the pulsed chromatographic regime.

Figure 1: Figure 1. Output curves in conducting a chemical reaction in the pulsed chromatographic regime.

If the distribution coefficients are unequal for at least one pair of starting substances, $b_i \neq b_j$, then after a certain time, required for separation of the corresponding bands, the reaction will cease. Conversely, a reaction requiring the participation of 2 or more molecules of a single substance ($nA \to B + C + ...$) is possible*, since in this case no splitting of the band of the starting substances will occur. Up to now we have considered the general case of chemical reactions proceeding in the chromatographic regime. Let us dwell in more detail on several particular cases:

a) Homogeneous reaction involving active impurities (inhibitors, initiators, and poisons):

$$nA(+X + Y) \to B + C,$$

where X and Y are active impurities.

With reversible sorption of X and Y and $b_A \neq b_X$, $b_A \neq b_Y$, the phenomena of inhibition and initiation must disappear because of the absence of X and Y in the A zone. The same is true in the case when acceleration or retardation of the reaction by any mechanism is caused by the reaction products. Positive and negative autocatalysis are equally impossible in chromatographic regime. The influence of the chromatographic regime on the features of chain reactions (limits, kinetics, etc.) deserves separate consideration.

Fig. 1. Output curves when conducting a chemical reaction in the pulsed chromatographic regime.
$a:\ b_A < b_B < b_C$ (in the absence of reaction); $b:\ b_A < b_B < b_C$; $v:\ b_A > b_B > b_C$; $g:\ b_B < b_A < b_C$

b) Heterogeneous catalysis in the presence of volatile contact poisons

$$\mathrm{A(+X + Y) \to B + C + \cdots}$$

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* A typical example of a bimolecular reaction feasible in the chromatographic regime is

$$\mathrm{HJ + HJ \to J_2 + H_2}.$$

In this case, reversible and irreversible adsorption of X and Y should be considered separately. With reversible adsorption, neither X nor Y will exert an influence because of their absence from the reaction zone.

With irreversible adsorption, the poisoning action of the poison will be limited to a zone determined by the amount of poison introduced in the injected portion and by the capacity of the catalyst with respect to the poison. After the band A has passed through the poisoned zone, the action of the poison will cease. Repeated introduction of the sample will lead to gradual broadening of the poisoned zone. Experiments of this kind make it possible to elucidate the nature of the poisoning action of the poison. Owing to the absence of products in the reaction zone, the kinetic regularities of heterogeneous catalysis are considerably simplified. Thus, in the kinetics of reactions on homogeneous and heterogeneous surfaces, the expressions for reaction rates contain no terms taking into account adsorption of products and reversible poisons (promoters). As a result, from the temperature dependence of the rate constant one obtains a value of the activation energy closer to the true one. In particular, for Langmuir kinetics, in E_{obs} the heats of adsorption of strongly adsorbing reaction products and reversible contact poisons disappear as additive terms. Depending on the coverage θ_A, two cases are possible:

$$E_{\text{obs chr}} = E_{\text{true}} - v_A Q_A \quad (\text{when } \theta_A \ll 1);$$
$$E_{\text{obs chr}} = E_{\text{true}} \quad (\text{when } \theta_A = 1),$$

where Q_A is the heat of adsorption of the reacting component A.

Thus, by carrying out the reaction by the usual stationary dynamic method and in the pulse-indicator variant of the chromatographic regime, one can reveal the influence of self-inhibition of the process by reaction products.

Above we considered the chromatographic regime for the case in which the rate of the catalytic reaction was considerably lower than the rate of adsorption. In a number of cases the rate of a heterogeneous catalytic process is determined by the rate of adsorption. Such reactions are conveniently studied by conducting them in a layer, in the chromatographic regime. For this purpose, a portion of one of the components of the initial reacting mixture is injected into the column. The course of the reaction will be determined by the sequence in which the reacting components are admitted and by the character of their bond with the surface. By changing this sequence, one can establish the true mechanism of the process. Especially promising is the combination of the tracer-atom method with chromatography.

In the near future it is intended to publish experimental data on the study of the regularities of catalytic processes conducted in the chromatographic regime.

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