JOURNAL OF CATALYSIS 95, 447–454 (1985)

Estimation of Kinetic Parameters of a Catalytic Reaction and Parallel Poisoning Reaction

R. E. MARDALEISHVILI AND YU. I. RAPOPORT

Department of Chemistry, Moscow State University, Moscow 117234, USSR

Received September 17, 1984; revised January 30, 1985

A method for kinetic analysis of catalytic reactions and accompanying catalyst poisoning reactions is suggested. The kinetic laws of these reactions are considered in the *n*th order form. The method allows one to determine the orders of reactions in each gas-phase reactant and in the surface concentration of active sites, and to find the rate constants of the main and poisoning reactions. The suggested way of obtaining and treating the experimental data provides the opportunity of a direct determination of a form of linear anamorphoses describing the data, and presents a criterion of their validity for a particular system. The possibilities of the method are illustrated by a kinetic investigation of the model reaction of acetylene cyclotrimerization on NbO_2. © 1985 Academic Press, Inc.

INTRODUCTION

The kinetics of catalytic reactions accompanied by poisoning are usually described in terms of empirical correlations. Such a description suffers, however, from the restricted applicability of these correlations (*1*). In contrast, the kinetic approach, involving independent experimental determination of kinetic parameters both for the main reaction and the poisoning reaction, provides much more information than does the choice of a proper empirical correlation, since the obtained kinetic equations represent the overall mechanism of a process.

During recent years the kinetic description of deactivation processes has been developed considerably. This is primarily due to Levenspiel's method (2) of determining some parameters of kinetic equations for a main reaction and an accompanying poisoning reaction carried out in flow reactor regime.

In the present work we suggest a new method for determination of parameters of kinetic equations which equally applies to studying catalytic reactions both in closed and flow systems (in continuos-flow stirred tank reactor, CSTR, regime).

RESULTS AND DISCUSSION

The *n*th order kinetic form of the reaction rates was shown (*2*) to be quite common for main and poisoning reactions both in the case of consecutive and parallel mechanisms of poisoning. Therefore, we suppose the kinetic laws to be as

$$W = -\frac{1}{\nu_i}\frac{dP_i}{dt} = \sigma k S^m \prod_i P_i^{n_i} \quad (1)$$

$$W_p = -\frac{dS}{dt} = \sigma k_p S^x \prod_i P_i^{y_i}, \quad (2)$$

where W is the rate of the reaction leading to the main products (main reaction), W_p is the rate of the poisoning reaction, P_i is the partial pressure of the ith component in the gaseous mixture, S is the concentration of active sites on a catalyst surface, k and k_p are the rate constants of main and poisoning reactions, respectively, per active site, σ is the surface area of a catalyst sample, ν_i is the stoichiometric coefficient of the ith component in the main reaction.

It should be noted that the necessary condition for applicability of Eqs. (1) and (2) is either the absence of the reaction products slowing down the main reaction, or their removal from the reaction area.

0021-9517/85 $3.00

Let the poisoning be considered as a result of irreversible blocking of catalytically active sites by products of a side reaction (blocking of the active sites by impurities as well as reversible blocking of the surface by main reaction products are not considered here).

As follows from Eqs. (1) and (2), the rate of a catalytic process is dependent, on the one hand, on the concentration (partial pressures) of reacting gases and, on the other hand, on the concentration of catalytically active sites characterizing the activity of a catalyst which we define as

$$A = -\frac{1}{\nu_i} \frac{dP_i/dt}{\prod_i P_i^{n_i}} = \sigma k S^m. \tag{3}$$

By comparing the relation between the activity and the active sites concentration (Eq. 3) to the kinetic law (Eq. 2) of a poisoning reaction, one can easily obtain the deactivation rate equation

$$-\frac{dA}{dt} = m\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k_\mathrm{p}}{k^{\frac{x-1}{m}}} \cdot A^{\frac{x-1}{m}+1} \cdot \prod_i P_i^{y_i}$$
$$= k_\mathrm{d} \cdot A^d \cdot \prod_i P_i^{y_i}, \tag{4}$$

where

$$k_\mathrm{d} = m\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k_\mathrm{p}}{k^{\frac{x-1}{m}}}$$

$$d = \frac{x-1}{m} + 1 \quad (d\text{—order of deactivation}).$$

Simple transformation of Eq. (4) gives

$$\ln\left(-\prod_i P_i^{-y_i} \cdot \frac{dA}{dt}\right) = \ln\left[m\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k_\mathrm{p}}{k^{\frac{x-1}{m}}}\right] + \left(\frac{x-1}{m}+1\right)\ln A$$
$$= \ln k_\mathrm{d} + d \ln A. \tag{5}$$

Linearizability of experimental data in coordinates

$$\ln\left(-\prod_i P_i^{-y_i} \cdot \frac{dA}{dt}\right) \text{—} \ln A$$

may be taken as a criterion of the validity of Eqs. (1) and (2) for the description of a given set of reactions at any degree of conversion.

If this condition is satisfied, the parameters of a straight line plotted in coordinates of Eq. (5) give information on the ratio of orders in active sites concentration for the main (m) and poisoning (x) reactions, on the one hand, and on the ratio of the rate constants of these reactions, on the other hand.

In order to present experimental data in coordinates of Eq. (5), the orders in gas-phase reactants for the main (n_i) and poisoning (y_i) reactions are required. These can be determined by means of any known technique (e.g., by measurement of initial rates of the main reaction and deactivation). However, in some cases it appears difficult to determine the orders by the initial rates measurement (e.g., when these initial rates are high or if the initial stage kinetics of a reaction are complicated by adsorption). Then the "concentration jump method" seems more appropriate.

The method consists of the following. A reaction is carried out to a certain arbitrarily chosen degree of conversion, then the partial pressure of one of the reactants is sharply changed within 1–2 s. In the case of a static system this may be easily realized by a pulse injection of an additional portion of a reactant into the system (from a reservoir containing the gas at a pressure higher than that of the reactant mixture in the system). Change in the partial pressure of a reactant affects the rates of the main reaction and deactivation. If the injection time is much less than the time required for reaction to proceed to a considerable conversion, then the catalyst poisoning in this time can be neglected, i.e., the catalyst activities, and consequently the concentration of active sites, immediately before (instant a) and just after (instant b) the injection can be taken to be equal. The rates W_a and W_b are determined by extrapolation of the $W = f(t)$ curve to the moment of injection. With this in mind, the following equation for determining the order of the main reaction in an injected component is obtained:

$$\lim_{t \to t^*_-} W = W_a = \left(\sigma k S^m \prod_{i \neq j} P_i^{n_i}\right) \cdot P_{ja}^{n_j};$$

$$\lim_{t \to t^*_+} W = W_b = \left(\sigma k S^m \prod_{i \neq j} P_i^{n_i}\right) \cdot P_{jb}^{n_j}$$

where t^* is the injection time,

$$n_j = \frac{\ln(W_a/W_b)}{\ln(P_{ja}/P_{jb})}. \tag{6}$$

This technique was successfully applied to determine the order of the cyclotrimerization of acetylene in benzene on NbO_2 accompanied by poisoning (*3*). It should be noted that the method appeared to be very useful in studying the reactions unaccompanied by poisoning, as well. Thus, for example, it was used to determine the orders in nitrogen and hydrogen of the ammonia synthesis reaction complicated by adsorption at an initial stage (*4*).

If the orders n_i in each reactant are known, Eq. (3) allows one to calculate the catalyst activity, A, at any time, and, consequently, to find the deactivation rate, $-dA/dt$.

The deactivation rate is related to partial pressures of reactants by Eq. (4). To determine the orders of the poisoning reaction in gas-phase reactants one can use "concentration jump method" experimental data. After differentiation of the respective A–t curves and extrapolation of the dA/dt–t dependence to the instant of injection from the left and right, the values of $(dA/dt)_a$ and $(dA/dt)_b$ can be obtained. These are related to the pressures of the components of a gaseous mixture by Eq. (4), which gives the following expression for the orders of a poisoning reaction in gas-phase reactants:

$$y_j = \frac{\ln\left[\left(\frac{dA}{dt}\right)_a \Big/ \left(\frac{dA}{dt}\right)_b\right]}{\ln(P_{ja}/P_{jb})}. \tag{7}$$

Performing the injections of each gas at different conversions, one can determine these orders throughout the reaction run.

Knowing the orders n_j and y_j, the experimental data can be represented in coordinates of Eq. (5) which allows one to determine the ratio of orders in active sites concentration for the main and poisoning reactions ($(x - 1)/m = d - 1$) directly from the experiment. As seen from its explicit form, this ratio may take various (both integer and fractional) values. In the same way, the values of orders of deactivation may be just as various as this ratio is (cf. Eq. (4)), which presents problems in determining these values by the choice of a proper correlation among a number of relationships suggested by Levenspiel (*2*) for analysis of deactivation kinetics in flow systems.

If a reaction is carried out in a CSTR and the stream composition can be considered as invariable in reaction ($P_{0i} - P_i \ll P_{0i}$; $P_{0i} \approx P_i = \text{const}$), then Eq. (4) gives direct information concerning the catalyst deactivation kinetics:

$$-\frac{dA}{dt} = m\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k'_p}{k^{\frac{x-1}{m}}} \cdot A^{\frac{x-1}{m}+1}, \tag{4.1}$$

where $k'_p = k_p \cdot \prod_i P_{0i}^{y_i}$.

From this it follows that

$$A^{-\frac{x-1}{m}} = A_0^{-\frac{x-1}{m}} + (x-1)\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k'_p}{k^{\frac{x-1}{m}}}\, t,$$

$$\text{if } x \neq 1 \tag{8}$$

$$\ln A = \ln A_0 - m\sigma k'_p t, \quad \text{if } x = 1. \tag{9}$$

The form of the linearized plot of activity as a function of the time of the catalyst exposure at constant composition of a gaseous mixture can be uniquely determined from the experimental data. It is sufficient for this to find the ratio $(x - 1)/m$ from the data linearized in coordinates $\ln(-dA/dt)$—$\ln A$:

$$\ln\left(-\frac{dA}{dt}\right) = \ln\left[m\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k'_{\mathrm{p}}}{k^{\frac{x-1}{m}}}\right] + \left(\frac{x-1}{m}+1\right)\ln A. \qquad (5.1)$$

It is noteworthy that Eqs. (8) and (9) can be easily reduced to the form of the linear correlations suggested by Levenspiel (*2*) for determining the order of deactivation. However, the choice of the best linearization, which is of key importance in determining the value of d according to Ref. (*2*), may be quite difficult, since it may appear unreliable to discriminate the best form of a linear anamorphosis for close values of d by the comparison of the correlation coefficients of the plots (or by any other way). In contrast, our method provides the possibility of the direct experimental determination of the order of deactivation

$$\left(d = \frac{x-1}{m} + 1\right)$$

relating with the mechanism of a process. This, in turn, gives a criterion of the validity of a linear anamorphosis of a given type as applied to a particular system.

Equation (5.1) can also be used for independent determination of the orders of a poisoning reaction in gas-phase reactants, y_i. For this purpose a series of experiments with gas streams of different compositions is needed that allows the comparison of the values of the intercepts found from Eq. (5.1) with the values of the varied partial pressures for each reactant:

$$\ln\left[m\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k'_{\mathrm{p}}}{k^{\frac{x-1}{m}}}\right] = \ln\left[m\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k_{\mathrm{p}}}{k^{\frac{x-1}{m}}}\right] + \sum_i y_i \ln P_{0_i}$$

$$y_i = \frac{\partial \ln\left[m\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k_{\mathrm{p}}}{k^{\frac{x-1}{m}}}\right]}{\partial \ln \bar{P}_{0_i}}. \qquad (7.1)$$

Using Eqs. (3) and (4) one can obtain the general form of a linear anamorphosis relating the catalyst activity to the amount of *j*th gaseous reactant spent in the reaction (providing a substantial excess of other reactants so that their partial pressures could be considered unvaried during the reaction run):

$$A^{-\left(\frac{x-1}{m}-1\right)} = A_0^{-\left(\frac{x-1}{m}-1\right)} + \frac{x-m-1}{\nu_j(y_j-n_j+1)}\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k_{\mathrm{p}}}{k^{\frac{x-1}{m}}} \cdot \prod_{i\neq j} P_i^{y_i-n_i} \cdot (P_{0_j}^{y_j-n_j+1} - P_j^{y_j-n_j+1}), \quad \text{if } m \neq x-1 \qquad (10)$$

$$\ln A = \ln A_0 - \frac{m}{\nu_j(y_j-n_j+1)} \cdot \frac{k_{\mathrm{p}}}{k^{\frac{x-1}{m}}} \cdot \prod_{i\neq j} P_i^{y_i-n_i} \cdot (P_{0_j}^{y_j-n_j+1} - P_j^{y_j-n_j+1}), \quad \text{if } m = x-1. \qquad (11)$$

For the *j*th component with $n_j = y_j$ Eqs. (10) and (11) reduce to

$$A^{-\left(\frac{x-1}{m}-1\right)} = A_0^{-\left(\frac{x-1}{m}-1\right)} + \frac{x-m-1}{\nu_j}\sigma^{-\left(\frac{x-1}{m}-1\right)} \cdot \frac{k_{\mathrm{p}}}{k^{\frac{x-1}{m}}} \cdot \prod_{i\neq j} P_i^{y_i-n_i} \cdot \Delta P_j, \quad \text{if } m \neq x-1 \qquad (10.1)$$

$$\ln A = \ln A_0 - \frac{m}{\nu_j} \cdot \frac{k_{\mathrm{p}}}{k} \cdot \prod_{i\neq j} P_i^{y_i-n_i} \cdot \Delta P_j, \quad \text{if } m = x-1. \qquad (11.1)$$

For a CSTR with a constant stream composition Eqs. (10) and (11) take the form

$$A^{-\left(\frac{x-1}{m}-1\right)} = A_0^{-\left(\frac{x-1}{m}-1\right)} + \frac{x-m-1}{\nu_j}\sigma^{-\left(\frac{x-1}{m}-1\right)} \frac{k_{\mathrm{p}}}{k^{\frac{x-1}{m}}} \cdot \prod_i P_{0_i}^{y_i-n_i} \cdot \int_0^t d(P_{0_j} - P_j(t)), \quad \text{if } m \neq x-1 \qquad (10.2)$$

$$\ln A = \ln A_0 - \frac{m}{\nu_j} \cdot \frac{k_p}{k} \cdot \prod_i P_{0_i}^{y_i - n_i} \cdot \int_0^t d(P_{0_j} - P_j(t)), \quad \text{if } m = x - 1. \quad (11.2)$$

It should be noted that Eqs. (10) and (11) relate the catalyst activity to the amount of a reactant spent in the reaction rather than to time that is characteristic of most of the existing kinetic descriptions of the processes accompanied by catalyst deactivation (*5–10*). Such an approach, in our opinion, reveals better the physical sense of the phenomenon and interrelation between the main and catalyst poisoning reactions.

Extrapolation of the experimental dependences of the activity on the amount of a component spent in the reaction in coordinates of Eqs. (10) and (11) to $P = P_0$ allows one to determine initial catalyst activity A_0 in a reaction under consideration.

Knowing the initial activities for catalysts with different surface concentrations of active sites and these concentrations (e.g., for diluted supported catalysts or for catalysts prepoisoned to a specified extent), the reaction order m can be found from

$$\ln A = \ln A_0 + m \ln S_0 \qquad (3.1)$$

and then the order x can be determined from known m and the ratio of m and x obtained from Eq. (5).

Equation (3) can also be used for determining the rate constant of a main reaction which, in turn, allows one to find the rate constant of a poisoning reaction from the ratio of these constants available from Eq. (5).

EXPERIMENTAL ILLUSTRATIONS

An experimental test of the method presented was carried out on the model reaction of acetylene trimerization in benzene on NbO_2 at 0°C (benzene was frozen in a trap through which the reacting gas, acetylene, was circulating). The "concentration jump" technique (see above) was applied to determine the orders in acetylene of the main (n) and poisoning (y) reactions for a wide range of pressures and conversions:

$$n = 1.0 \pm 0.1$$

$$y = 1.0 \pm 0.1$$

With this in mind, relation (5) between the deactivation rate and catalyst activity takes the form

$$\ln\left(-\frac{1}{P}\frac{dA}{dt}\right) = \ln\left[m\sigma^{-\left(\frac{x-1}{m}-1\right)} \frac{k_p}{k^{\frac{x-1}{m}}}\right] + \left(\frac{x-1}{m} + 1\right) \ln A, \quad (5.2)$$

where P is the pressure of acetylene within the reaction system.

Experimental data plotted in coordinates of Eq. (5.2) are presented in Fig. 1. As seen from the figure, the process clearly splits into two stages. As was shown earlier (*11*), the stages, characterizing the process on the whole, differ in the way of catalytic deactivation. It was determined that at 0°C the transition from stage I to stage II takes place when the growth of coke deposits is completed and the newly formed hydrocarbonaceous monolayer starts functioning as a catalyst. The stage-I deactivation is caused by the blocking of the NbO_2 surface by the coke deposits. The stage-II deactiva-

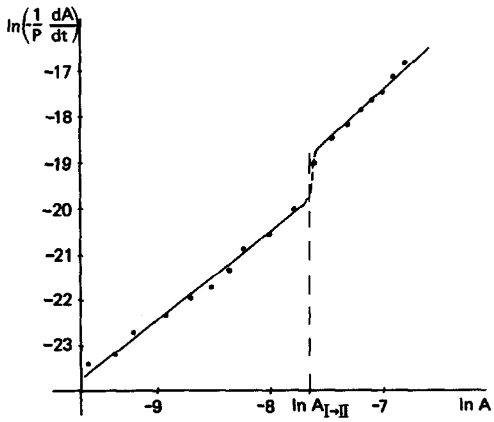

FIG. 1. Determination of the ratios of the orders in active sites concentration for the main and poisoning reactions (in the process of trimerization of acetylene on NbO_2 at 0°C).

tion is caused by gradual deactivation of these deposits.

The slopes of the straight lines (Fig. 1) characterize the ratios of orders in active sites concentration for the main and poisoning reaction at the stages I and II. The values of intercepts (at $\ln A = 0$) characterize, other things being equal, the ratios of the rate constants of these reactions for each stage.

Figure 1 demonstrates that these ratioes for the stages I and II are different. This fact indicates the splitting of the process into two stages with different kinetic laws.

The determined ratios are

$$\text{at stage I } \frac{x_{\text{I}} - 1}{m_{\text{I}}} + 1 = 2.25 \pm 0.10$$

$$\text{at stage II } \frac{x_{\text{II}} - 1}{m_{\text{II}}} + 1 = 2.00 \pm 0.10,$$

that is equivalent to $x_{\text{II}} = m_{\text{II}} + 1$.

The kinetic laws are

$$\text{at stage I} \begin{cases} -\dfrac{dP}{dt} = \sigma k_{\text{I}} S^{m_{\text{I}}} \cdot P \\ -\dfrac{dS}{dt} = \sigma k_{\text{Ip}} S^{1.25 m_{\text{I}}+1} \cdot P \end{cases}$$

$$\text{at stage II} \begin{cases} -\dfrac{dP}{dt} = \sigma k_{\text{II}} S^{m_{\text{II}}} \cdot P \\ -\dfrac{dS}{dt} = \sigma k_{\text{IIp}} S^{m_{\text{II}}+1} \cdot P \end{cases}$$

The transition from stage I to stage II, reflected in coordinates

$$\ln\left(-\frac{1}{P}\frac{dA}{dt}\right) \text{—} \ln A,$$

is represented by a "shoulder" connecting the segments of the straight lines (Fig. 1). This "shoulder" indicates the quantative change in the deactivation rate $(-dA/dt)$, corresponding to the qualitive changes in the deactivation mechanism characterizing the process at the stages I and II. The location of the "shoulder" depends on the catalytic activity in the transition region ($A_{\text{I}\rightarrow\text{II}}$). The $A_{\text{I}\rightarrow\text{II}}$ value, in its turn, other things being equal, depends on the NbO_2 catalyst surface area.

The results obtained and Eqs. (10) and (11) can be summarized in a form of linear anamorphoses, representing the experimental data at stages I and II, respectively:

$$A^{-0.25} = A_0^{-0.25} + \alpha_{\text{I}} \Delta P_{\text{I}},$$

where

$$\alpha_{\text{I}} = 0.25 m_{\text{I}} \sigma^{-0.25} \cdot \frac{k_{\text{pI}}}{k_{\text{I}}^{1.25}};$$

$$\Delta P_{\text{I}} = \Delta P \quad (10.3)$$

$$\ln A = \ln A_{0\text{II}} - \alpha_{\text{II}} \Delta P_{\text{II}},$$

where

$$\alpha_{\text{II}} = m_{\text{II}} \frac{k_{\text{pII}}}{k_{\text{II}}}; \quad A_{0\text{II}} = A_{\text{I}\rightarrow\text{II}};$$

$$\Delta P_{\text{II}} = \Delta P - \Delta P_{\text{I}\rightarrow\text{II}}. \quad (11.3)$$

The experimental data plotted in coordinates of Eqs. (10.3) and (11.3) are presented in Fig. 2.

Thus, the suggested method allowed us to find the reaction orders or their ratios in the reaction studied, and to determine directly the form of the catalytic decay linear

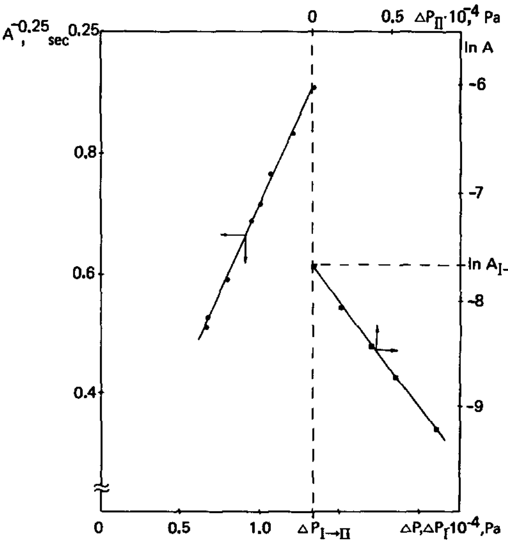

FIG. 2. Linear anamorphoses relating the NbO_2-catalyst activity to the amount of acetylene spent in the reaction at stages I and II.

anamorphoses without their empirical selection.

It is noteworthy that quite a number of empirical and semiempirical correlations used by various authors to describe the kinetics of catalytic processes accompanied by poisoning comprise different particular cases of Eqs. (10) and (11).

Consider some other examples.

1. Hydrogenation of benzalaniline on Pt/SiO_2 (*7*) is described well by equation

$$\lg \frac{\frac{1}{\beta} Z_0 - B_0 + B}{B} = (Z_0 - \beta B_0) \frac{kt}{2.3} + \lg \frac{Z_0}{\beta B_0}$$

which takes place if

$$Z = Z_0 - \beta(B_0 - B) = Z_0 - \beta \Delta B, \quad (12)$$

where Z and B are the concentrations of active sites and reactant, respectively.

Equation (12) represents a particular case of Eq. (10) at $x = m$ and $y = n$. Comparing Eqs. (12) and (10) within this condition in mind, one can easily realize that the parameter entering Eq. (12) is $\beta = k_p/k$.

2. Hydrogenation of cyclopentane on Pd/Al_2O_3 (*8*) is described by the following relations:

(a) at temperatures below 320°C

$$r_B = ka$$

$$-\frac{da}{dt} = k_d(C_B)^p a^2 = k'_d a^2,$$

where r_B is the rate of hydrogenation, k is the rate constant of the main reaction, a is the catalyst activity at instant t, $a = W_t/W_0$, C_B is the concentration of cyclopentane, k_d is the deactivation rate constant, and k'_d is the effective deactivation rate constant at a constant composition of the gaseous mixture.

These relations reduce to the equation

$$\ln a = \ln a_0 - \alpha \Delta B. \quad (13)$$

Equation (13) is a particular case of Eq. (11) at $x = m + 1$ and $y_{ef} = n$. Comparison of Eqs. (11) and (13) gives $\alpha = m \frac{k_p}{k}$;

(b) at temperatures above 320°C

$$r_B = ka$$

$$\frac{da}{dt} = k_d(C_B)^p a^3 = k'_d a^3.$$

This set of equations reduces to

$$\frac{1}{a} - \frac{1}{a_0} = \alpha \Delta B \quad (14)$$

which represents a particular case of Eq. (10) at $x = 2m + 1$, $y = n$. The comparison of Eqs. (10) and (14) gives $\alpha = m \frac{k_p}{k^2}$.

The above examples illustrate the possibilities of the kinetic approach in studying the reactions accompanied by poisoning.

The suggested method of obtaining and treating the experimental data provides the possibility of a direct determination of a form of linear anamorphoses describing the data, and presents a criterion of their validity for a particular system. The method allows one to determine the orders of reactions in each gas-phase reactant and in the surface concentration of active sites, to find the rate constants of the main and poisoning reactions, and to reveal the physical sense of parameters entering the empirical equations proposed earlier.

REFERENCES

1. Buyanov, R. A., "Coke Formation and Regeneration of Dehydrogenation Catalysts in the Production of Synthetic Rubber Monomers." Nauka, Moscow, 1968.

2. Levenspiel, O., *J. Catal.* **25,** 265 (1972).

3. Mardaleishvili, R. E., Rapoport, Yu. I., Keroglu, E. V., and Keroglu, A. Kh., *Vestn. Mosk. Univ. Ser. 2: Khim.* **21,** 354 (1980).

4. Mardaleishvili, R. E., and Smorodinskaya, Zh. Ya., *in* "Proceedings, 3rd All-Union Conference on Catalytic Reaction Mechanisms," p. 101. Novosibirsk, 1982.

5. Jossens, L. W., and Petersen, E. E., *J. Catal.* **73,** 377 (1982).

6. Davis, S. M., and Somorjai, G. A., *J. Catal.* **65,** 78 (1980).

7. Lebedev, V. P., and Strel'nikova, Zh.V., *Nauchn. Dokl. Vyssh. Shk.* **2,** 260 (1959).
8. Fuentes, S., and Figueras, F., *J. Catal.* **54,** 397 (1978).
9. Rosental, A. L., and Naberezhnova, G. N., *Kinet. Katal.* **15**(1), 190 (1974).
10. Levinter, M. E., Berkovich, L. M., Kurchatkina, T. V., and Panfilov, N. A., *Kinet. Katal.* **16,** 797 (1975).
11. Mardaleishvili, R. E., and Rapoport, Yu. I., *Dokl. Akad. Nauk SSSR* **277,** 416 (1984).