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ON THE ANALYSIS OF KINETIC MODELS FOR CATALYTIC REACTIONS

By

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Abstract

Variations in reaction rates and selectivities with conversion, temperature, pressure, dilution, and reaction mixture composition have been discussed for kinetic models of various forms and characters. The possibilities of a preliminary analysis of experimental data have been shown for the kinetic models under study.

At present, the determination of adequate kinetic models for various processes is considered a key problem of chemical kinetics in heterogeneous catalysis. An important step in establishing these models should be a preliminary analysis of experimental data directed towards the discrimination of inadequate kinetic characteristics and selection of the most unambiguous description. Methods of this preliminary analysis have been developed[1~6] to reveal the effect of various parameters on the initial process rate, kind of kinetic characteristics, and process selectivity. The analysis is generalized in this paper and its employment has been discussed. The analysis covers both single-route and multiple-route systems.[7,8]

1. Principal Backgrounds

Let us consider a system of components $A_1, A_2, \cdots, A_1', A_2', \cdots$, involving a steady-state reaction described by different stoichiometric routes :[9]

$$\begin{aligned} \nu_1 A_1 + \nu_2 A_2 &= \nu_3 A_3 + \nu_4 A_4 , \\ \nu_1' A_1 + \nu_2' A_2 &= \nu_3' A_3' + \nu_4' A_4' , \end{aligned} \qquad (1)$$

(stoichiometric coefficients $\nu_1, \cdots, \nu_4'$ can be positive, negative or equal to zero for a parallel, consecutive or parallel-consecutive character of the conversion, respectively).

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Reaction rate for each of i-th routes can be expressed by a general kinetic equation:

$$r_i = k_i \frac{\Pi P_j^{n_{ij}}}{\Pi_m z_{im}^{l_{im}}} \gamma_i , \qquad (2)$$

where P_j is partial pressure of the components ($j=1, \cdots$), n_{ij} and l_{im} are positive, negative or zero exponents, respectively, and γ_i is coefficient of reversibility for the reaction following the i-th route[10] expressed as

$$\gamma_i = 1 - (\psi_i / K_i)^{1/\sigma_i} , \qquad (3)$$

where σ_i, K_i and ψ_i are, respectively, stoichiometric number of the rate-determining step[7] or a mean stoichiometric number[8], equilibrium constant, and the expression of mass action law for the equilibrium in the given route where running reaction component concentrations are substituted for equilibrium concentrations. The denominator of Eq. (2) includes a z_{im} value which, in the simplest case, is a polynomial

$$z_{im} = C_{im} + \sum_j k_{imj} P_j , \qquad (4)$$

where $C_{im}=0$ or $C_{im}=1$ while k_{imj} values are adsorption coefficients or complex expressions containing step rate constants:

$$k_{imj} = (k_0)_{imj} \, e^{\pm q_{imj}/RT} , \qquad (5)$$

where q_{imj} are heat effects or algebraic sums of activation energies of the steps. More complicated expressions of kinetic relationships than those in Eq. (2)–(5) are very rare and can be neglected.

Eq. (2) holds for expressing the rate of a complex reaction proceeding by each of the routes in the following cases:

(i) the reaction is irreversible for all routes ($\gamma_i=1$);
(ii) the reaction is in equilibrium for all routes except one;[11]
(iii) the reaction follows different routes having no common steps;
(iv) only fast (quasi-equilibrium) steps are common for different reaction routes.[12]

The effect of process conditions on reaction rate for each i-th route can also be expressed as a product:[1]

$$r_i = r_{0i} \, \phi_i(x_i) \, \gamma_i \qquad (6)$$

where r_{0i} is initial reaction rate (reaction "level") at $x_i = 0$ and $\phi_i(x_i)$ is a dimensionless function of reaction conversion x_i for a given route determined by a form of a kinetic equation. The r_{0i} value is dependent on

both the form of kinetic equation and initial process conditions. In this case, the following restrictions are imposed on relationship :[6]

$$r_i = r_{0i} > 0 \qquad \text{at } x_i = 0\,, \tag{7}$$

$$r_i = 0 \qquad \text{at } x_i = 1 \text{ and } \gamma_i = 1 \qquad \text{or at } \gamma_i = 0\,. \tag{8}$$

Selectivity at a given catalyst activity is the most essential characteristic of a process following different stoichiometric routes (*i. e.* described by different stoichiometric equations.[8,9] It is defined as a ratio between an algebraic sum of reaction rates for all independent routes leading to the formation of the j^*-th product and a sum of reaction rates for all routes of conversion of the initial substance.[2] This is equivalent to a ratio of desirable product accumulation rate (W_{j^*}) to total conversion rate (W_1) of the initial substance (A_1) :

$$S = W_{j^*}/W_1\,. \tag{9}$$

Let us consider a sufficiently common case where a by-product is formed from and in parallel with desirable product (consecutive-parallel scheme). Considering expression (9), we obtain :

$$S = \frac{1-\beta}{1+\alpha} \cdot \frac{\dfrac{\phi_{(j^*+1)}\gamma_{(j^*+1)}}{\phi_1\gamma_1}}{\dfrac{\phi_{i'}\gamma_{i'}}{\phi_1\gamma_1}}\,, \tag{10}$$

where

$$\alpha = r_{0i'}/r_{01}\,, \tag{11}$$

$$\beta = r_{0(j^*+1)}/r_{01}\,, \tag{12}$$

j^*+1 index defines the route of further conversion of the desirable product (A_{j^*}), and i' defines all parallel routes of conversion of initial substances. When $\beta=0$ and $\alpha=0$, expression (10) holds true for a parallel and consecutive scheme, respectively. In this case, the following restrictions are imposed on the dependence of selectivity on conversion of the initial substance for a consecutive reaction scheme :

$$S = 1 \qquad \text{when } x_1 = 0\,, \tag{13}$$

$$0 < S < 1 \qquad \text{when } x_1 = 1\,. \tag{14}$$

In contrast, a parallel scheme is characterized by $0<S<1$ both for $x_1+x_2=0$ and $x_1+x_2=1$ (where x_1 and x_2 are conversions for the two directions, respectively).

The above relationships offer a possibility of analysing the changes in reaction rates and selectivities, *i. e.* their kinetic characteristics, for varying process conditions according to the character of kinetic models. It is assumed here that no changes in the process mechanism, and hence in the form of kinetic equations, are involved within the region of variation of process conditions —temperature (T), pressure (P), dilution of reaction mixture with an inert substance ($\delta=P_{\text{in}}/P_{\text{i}}^{0}$), and conversion.

2. Effect of Process Conditions on Kinetic Characteristics

An analysis of changes in reaction rates and selectivities with temperature, pressure, dilution, and initial composition at a constant conversion can be a source of useful information for constructing kinetic models. It is expedient here to place particular emphasis on revealing the extremes.

Optimum characteristics for a multiple-route reaction[4] are determined by the expression

$$\frac{\partial \ln W_{j^*}}{\partial Y}=\frac{\partial \ln W_1}{\partial Y}, \tag{15}$$

from which a relation can be derived for a two-route reaction:

$$\frac{\partial \ln r_1}{\partial Y}=\frac{\partial \ln r_2}{\partial Y}, \tag{16}$$

where Y is the parameter under investigation and r_1 and r_2 are reaction rates for the routes of desirable product and by-product formation respectively.

Based on these expressions and also on (7), (8), (13), and (14), it is possible to analyse how the variations of any process parameter affect the kinetics of the process as will be done below. The analysis will be carried out for a selectivity of a two-route reaction. Moreover, optimum rate conditions for a single route reaction can also be found from this analysis when $r_2=0$. It should be emphasized that condition (13) enable one to conclude whether a parallel or a consecutive reaction scheme is involved. If variations of process conditions tend to change the initial selectivity value extrapolated to $x_1=0$, it suggests a parallel reaction scheme. If the initial selectivity value remains to be equal to unity (or about) even though the process conditions are varied, it may be concluded that the reaction proceeds by a consecutive scheme.

(*a*) *Effect of Temperature*

The occurrence of a temperature optimum for selectivity of a two-route

reaction within the temperature range under study ($T_{min}<T<T_{max}$) is evident from Eqs. (2) and (16) when $m=1$ and the following condition is true:[4]

$$(H)_{T_{min}}<E_1-E_2<(H)_{T_{max}}, \tag{17}$$

where

$$H=\frac{l_2h_2}{z_2}-\frac{l_1h_1}{z_1}+\frac{(1-\gamma_1)Q_1}{\sigma_1\gamma_1}-\frac{(1-\gamma_2)Q_2}{\sigma_2\gamma_2}, \tag{18}$$

$$h_i=\sum_j k_{ij}q_{ij}P_j, \qquad (i=1, 2), \tag{19}$$

E_1 and E_2 are reaction activation energies for route 1 and route 2, respectively, and Q_1 and Q_2 are their heat effects. Expressions (17)~(19) also hold as extremity conditions for a single-route reaction when $E_2=Q_2=h_2=0$.

Expressions (17)~(19) make it possible to relate experimental data to the type of kinetic models. In Figs. 1 and 4, temperature dependences of reaction rate and selectivity, respectively, are plotted for kinetic models of different forms. It is seen that different forms of kinetic models exhibit different rate-temperature and selectivity-temperature plots which make it

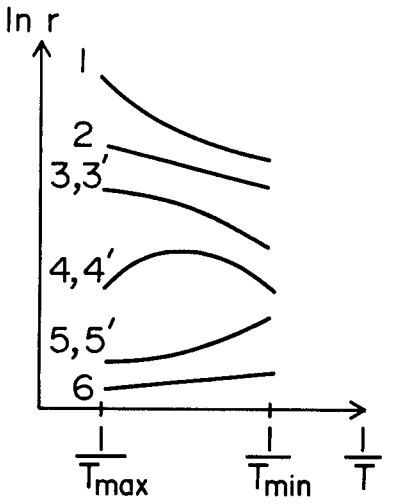

Fig. 1. Plot of reaction rate *vs.* temperature at a constant reaction mixture composition and different forms of kinetic models in Arrhenius-like coordinates for endothermal and irreversible exothermal reactions (1-6) and reversible exothermal reactions (3′~5′):

1, $h>0$; 2, $\gamma=1$ at $l=0$ or $h=0$; 3, $h<0$ at $E>(H)r_{max}$; 4, $h<0$ at $(H)r_{min}<E<(H)_{max}$; 5, $h<0$ at $E<(H)r_{min}$; 6, $E<0$ at $\gamma=1$ and $l=0$ or $h=0$; 3′, $E>Hr_{max}$; 4′ $(H)r_{min}<E<(H)r_{max}$; 5′, $E<(H)r_{min}$.

possible to tentatively estimate the kinetics of the reaction.

(*b*) *Effect of Pressure*

Extreme dependence of process selectivity on pressure (P) is found to be possible for a certain stoichiometry of the reaction and a certain relation between the exponents of kinetic equations for the routes. For a two-route reaction, Eqs. (2) and (16), when $m=1$, give the following conditions for the occurrence of selectivity maximum :[4]

$$\begin{aligned} &\Delta\nu_1 > \Delta\nu_2 , \\ &\sum_j n_{1j} - l_1 > \sum_j n_{2j} - l_2 \end{aligned} \tag{20}$$

or

$$\begin{aligned} &\Delta\nu_1 < \Delta\nu_2 , \\ &\sum_j n_{ij} - l_1 < \sum_j n_{2j} - l_2 , \end{aligned} \tag{21}$$

where $\Delta\nu_1=\nu_3+\nu_4-\nu_1-\nu_2$ and $\Delta\nu_2=\nu_3'+\nu_4'-\nu_1'-\nu_2'$ while $\sum_j n_{1j}$ and $\sum_j n_{2j}$ are sums of exponents at partial pressures of the components in kinetic equations for routes 1 and 2 respectively, the desirable product being formed in the first route of system (1). When $\Delta\nu_2=\sum_j n_{2j}=l_2=0$, expressions (20) and (22) simplify to conditions of extreme rate/pressure dependence for a single route reaction. The consideration of pressure dependences of process rate and selectivity can be reduced to the analysis of their variations due to dilution (δ) of an initial mixture.[5]

If conditions (20) and (21) fail to be satisfied, different variations in process pressure and selectivity are possible depending on the form of kinetic models. These variations are plotted in Figs. 2 and 4. Conclusions concerning kinetics of a process based on these plots can be readily drawn from experimental results.

(*c*) *Effect of Initial Composition of Reaction Mixture*

When varying the composition of a reaction mixture (ρ) for a two-route reaction, the selectivity can pass through a maximum if the following conditions are satisfied for Eq. (2) type :

$$\begin{aligned} &\sum_j n_{1j} - n_{12} > \sum_j n_{2j} - n_{22} , \\ &\sum_j n_{1j} - l_1 > \sum_j n_{2j} - l_2 \end{aligned} \tag{22}$$

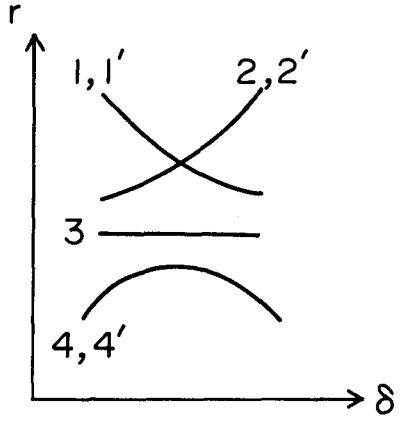

Fig. 2. Plot of reaction rate *vs.* dilution for irreversible (1~4) and reversible (1′, 2′, 4′) reactions:

1, $\sum_j n_j > l$ at $z = \sum_j k_j P_j$ or $\sum_j n_j \geq l$ at $z = 1 + \sum_j k_j P_j$; 2, $\sum_j n_j < l$ at $z = \sum_j k_j P_j$; 3, $\sum_j n_j = l$ at $z = \sum_j k_j P_j$; 4, $\sum_j n_j < l$ at $z = 1 + \sum_j k_j P_j$; 1′, $\sum_j n_j \geq l$ at $\Delta\nu < 0$; 2′, $\sum_j n_j \leq l$ at $\Delta\nu > 0$; 4′, $\sum_j n_j < l$ at $\Delta\nu < 0$ or $\sum_j n_j > l$ at $\Delta\nu > 0$.

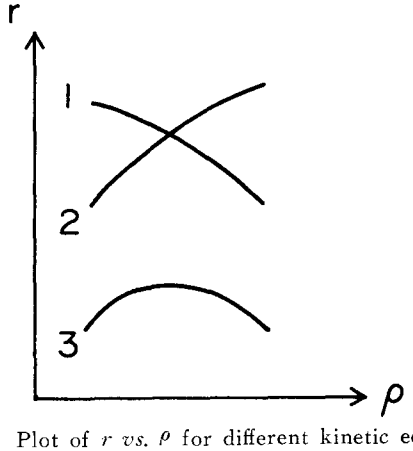

Fig. 3. Plot of r *vs.* ρ for different kinetic equations:

1, (a) P_2 is in both numerator and denominator, $\sum_j n_j > n_2$ at $l > \sum_j n_j$; (b) P_2 in denominator only, $\sum_j n_j \leq l$; 2, (a) P_2 both in numerator and denominator, $\sum_j n_j < n_2$ at $l < \sum_j n_j$; (b) P_2 in numerator only, $\sum_j n_j > n_2$ at $l < \sum_j n_j$ or $\sum_j n_j < n_2$ at $l > \sum_j n_j$; (c) P_2 is not contained in equation, $\sum_j n_j > l$; (d) power equation, $\sum_j n_j < n_2$; 3, (a) P_2 both in numerator and denominator, $\sum_j n_j > n_2$ at $l < \sum_j n_j$ or $\sum_j n_j < n_2$ at $l > \sum_j n_j$; (b) P_2 in denominator only, $\sum_j n_j > n_2$; (c) P_2 in numerator only, $\sum_j n_j > n_2$ at $l > \sum_j n_j$ or $\sum_j n_j < n_2$ at $l < \sum_j n_j$; (d) P_2 is not contained in equation $\sum_j n_j < l$; (e) power equation, $\sum_j n_j > n_2$.

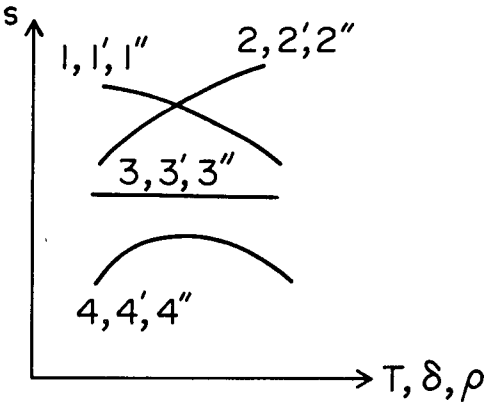

Fig. 4. Plot of selectivity *vs.* temperature (1~4), dilution δ (1'~4'), and reaction mixture composition ρ (1''~4'') for the following cases:

1, $E_1-E_2<(H)r_{\min}$; 2, $E_1-E_2>(H)r_{\max}$; 3, $E=E_2$ at $H=0$ or $E_1=E_2$ at $l_1=l_2=0$ and $\gamma_1=\gamma_2=1$; 4, $(H)r_{\min}<E_1-E_2<(H)r_{\max}$; 1', $\sum_j n_{1j}-l_1$ at $H=0$ $\sum_j n_{2j}-l_2$ at $\Delta\nu_1<\Delta\nu_2$; 2', $\sum_j n_{1j}-l_1<\sum_j n_{2j}-l_2$ at $\Delta\nu_1>\Delta\nu_2$; 3', $\sum_j n_{1j}-l_1=\sum_j n_{2j}-l_2$; 4', $\sum_j n_{1j}-l_1<\sum_j n_{2j}-l_2$ at $\Delta\nu_1<\Delta\nu_2$ or $\sum_j n_{1j}-l_1>\sum_j n_{2j}-l_2$ at $\Delta\nu_1>\Delta\nu_2$; 1'', $\sum_j n_{1j}-n_{12}>\sum_j n_{2j}-n_{22}$ at $\sum_j n_{1j}-l_1<\sum_j n_{2j}-l_2$; 2'', $\sum_j n_{12}-n_{12}<\sum_j n_{2j}-n_{22}$ at $\sum_j n_{1j}-l_1>\sum_j n_{2j}-l_2$; 3'', $\sum_j n_{1j}=\sum_j n_{2j}$ at $l_1=l_2$; 4'', $\sum_j n_{1j}-n_{12}>\sum_j n_{2j}-n_{22}$ at $\sum_j n_{1j}-l_1>\sum_j n_{2j}-l_2$ or $\sum_j n_{1j}-n_{12}<\sum_j n_{2j}-n_{22}$ at $\sum_j n_{1j}-l_1<\sum_j n_{2j}-l_2$.

or

$$\sum_j n_{1_j}-n_{12}<\sum_j n_{2_j}-n_{22}\,,$$
$$\sum_j n_{1_j}-l_1<\sum_j n_{2_j}-l_2\,, \qquad (23)$$

where n_{12} and n_{22} are exponents in kinetic equations of routes 1 and 2, respectively, for the component being in excess. In a single-route process, expressions (22) and (23) are also conditions of extreme reaction rate with regard to ρ when $\sum n_{2j}=n_{22}=l_2=0$. If conditions (22) and (23) fail to be satisfied various reaction rates and selectivities as a function of ρ are possible as is illustrated in Figs. 3 and 4. The different character of these relationships indicates a possibility of revealing kinetic laws by analysing these dependences.

3. The Effect of Conversion on Kinetic Characteristics

In a multiple-route reaction, the variation in selectivity with conversion will be different for parallel and consecutive schemes and for different kinetic

models. The following dependences of selectivity on conversion occur for a parallel process scheme: selectivity increases with conversion if reaction rate order for the main route is lower than that for the by-product formation route (in case of power kinetic equations or those of Eq. (2) type with identical denominators for the two routes) or the reaction rate in the second route is strongly inhibited by the products; selectivity is independent of conversion where the structure of kinetic equations for the routes is similar or when $\alpha \approx 0$. In a consecutive process, a constant selectivity with changing conversion is indicative of higher reaction rate orders for the side route (in case of power kinetic equations or those of Eq. (2) type with identical denominators for the routes), or strong reaction inhibition in the by-product route in case of non-power equation. A similar case is when $\beta \approx 0$ or the reaction rate in all the routes is described by a zero-order equation. A decreasing $S(x)$ relation is characteristic of the two process schemes where the reaction rate order for the main route is higher than that for the side route (in case of power kinetic equation), or reaction rate is strongly inhibited by the products in the main product formation route. These $S(x)$ dependences are plotted in Fig. 5 and offer a means for revealing kinetic laws governing complex processes.

It is seen from the analysis of reaction rate as a function of conversion for a process involving only one stoichiometric route that different forms of kinetic models are critical for the shape of such conversion curves.[1,6] Convex conversion curves indicate a slight dependence of reaction rate on the concentration of initial components whereas concave conversion curves indicate either high orders for initial components or reaction rate inhibition by the products. The analysis of the second reaction rate derivative from conversion $(\partial^2 r/\partial x^2)_{x=0}$ leads to the following expression:[6]

$$z_0\left[(1+\rho+\delta)\,\nu_2 \sum_{j'} n_{j'} + \Delta\nu\left(n_1 \frac{\nu_2}{\nu_1} + n_2 \rho\right)\right] \lessgtr$$

$$\lessgtr l\left[\Delta\nu(z_0-1) - P\sum_j k_j \nu_j\right]\left[\left(\rho + \frac{\nu_2}{\nu_1}\right) z_0 + \frac{\rho}{1+\rho+\delta}\left(\Delta\nu + P\sum_j k_j \nu_j\right)\right], \tag{24}$$

where $z_0 = z(x)_{x=0}$; $\sum_j k_j \nu_j = k_3\nu_3 + k_4\nu_4 - k_1\nu_1 - k_2\nu_2$; $j' = 1, 2$. The inequality signs ($<$ and $>$) in expression (24) point to a convex or concave form of conversion curves, respectively, while the equality sign indicates that the reaction rate is independent of conversion.

It follows from expression (24) that a character of the $r(x)$ function is determined by a form of kinetic equations and their constants ratios as well

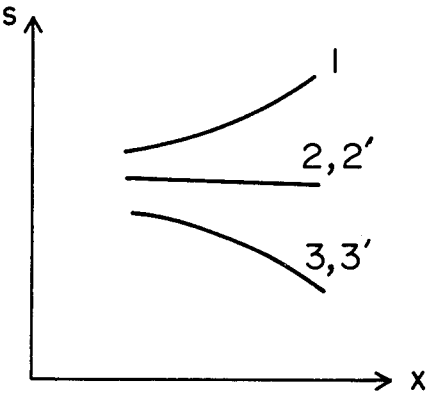

Fig. 5. Plot of selectivity *vs.* conversion for a two-route reaction with a parallel (1~3) and consecutive (2′, 3′) schemes of conversion:

1, (a) power equations, $\sum_j n_{1j} < \sum_j n_{2j}$; (b) z_1 and z_2 contain products, $\sum_j n_{1j} < \sum_j n_{2j}$ at $l_1 \leqslant l_2$ or $\sum_j n_{1j} > \sum_j n_{2j}$ at $l_1 \ll l_2$; (c) z_1 and z_2 contain no products, $\sum_j n_{1j} > \sum_j n_{2j}$ at $l_1 \geqslant l_2$ or $\sum_j n_{1j} < \sum_j n_{2j}$ at $l_1 \gg l_2$; 2, (d) $\sum_j n_{1j} = \sum_j n_{2j}$ at $l_1 = l_2$ or $\alpha \approx 0$; 3 and 3′ (a) power equations, $\sum_j n_{1j} > \sum_j n_{2j}$; (b) z_1 and z_2 contain products, $\sum_j n_{1j} > \sum_j n_{2j}$ at $l_1 \geqslant l_2$ or $\sum_j n_{1j} < \sum_j n_{2j}$ at $l_1 \gg l_2$; (c) z_1 and z_2 contain no products, $\sum n_{1j} < \sum_j n_{2j}$ at $l_1 \leqslant l_2$ or $\sum_j n_{1j} > \sum_j n_{2j}$ at $l_1 \ll l_2$; 2′, (a) power equations, $\sum_j n_{1j} < \sum_j n_{2j}$; (b) z_1 and z_2 contain products, $\sum_j n_{1j} < \sum_j n_{2j}$ at $l_1 \leqslant l_2$ or $\sum_j n_{1j} > \sum_j n_{2j}$ at $l_1 \ll l_2$; (c) z_1 and z_2 contain no products, $\sum_j n_{1j} > \sum_j n_{2j}$ at $l_1 \geqslant l_2$ or $\sum_j n_{1j} < \sum_j n_{2j}$ at $l_1 \gg l_2$; (d) $\sum_j n_{1j} = \sum_j n_{2j} = l_1 = l_2 = 0$ or $\beta \approx 0$.

as reaction conditions. It follows, then, that varying initial process conditions may result in essential changes in the form of the $r(x)$ function which will correspondingly affect the form of kinetic equation. It virtually means a possible transition of a kinetic equation to its particular cases, when the variations of initial conditions are sufficiently great, and the effect of these variations on the shape of conversion curves. It appears, then, that these variations should be considered when analysing experimental evidence which has, therefore, to be obtained within a sufficiently broad range of process parameters.

It can be seen that an analysis of selectivity and reaction rate dependences on reaction conditions and conversion gives an insight into the properties of kinetic models.

4. Analysis of Kinetic Models of Some Reactions

The potentialities of the above approach can be illustrated by the analy-

sis of kinetic models for some reactions studied by our laboratory in gradientless systems.

Dehydrogenation of isopentenes over a calcium-nickel phosphate catalyst.

This process occurs to form isoprene, cracked products, and small amounts of coke.[13] Kinetic studies of the reaction proceeding in a temperature range of 580 to 650°C and with diluting isopentenes with steam (δ was 10 to 30) showed that variations in process conditions at low conversions result in selectivity changes which indicate a parallel reaction scheme:

$$i\text{-}C_5H_{10} = C_5H_8 + H_2\,, \tag{25}$$

$$i\text{-}C_5H_{10} = \text{cracked products}\,. \tag{26}$$

Selectivity of this process is practically independent of conversion for x being from 0.1 to 0.6 and represented by straight line 2 in Fig. 5 which corroborates a parallel reaction scheme and describes the condition: $\sum_j n_{1j} = \sum_j n_{2j}$ at $l_1 = l_2$. Selectivity as a function of temperature and dilution at a constant composition of reaction mixture is described by curves 1 and 3′, respectively, in Fig. 4 characterized by the conditions: $E_1 - E_2 < (H)_{T_{\min}}$, $\sum_j n_{1j} - l_1 = \sum n_{2j} - l_2$ and indicating that the kinetics of this reaction is similar for the two routes.

Temperature and dilution dependences of the reaction for the two routes

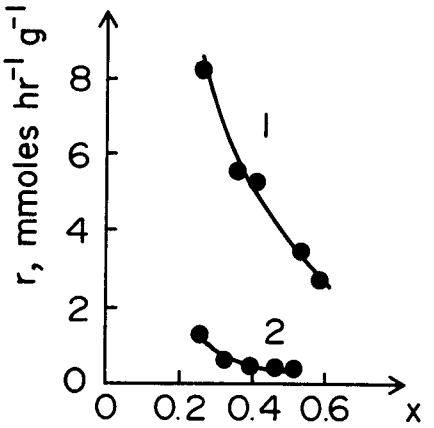

Fig. 6. Conversion curves of isopentene dehydrogenation at $T = 600$°C and $\delta = 30$[13]:

1, isoprene formation route;
2, cracked products formation route.

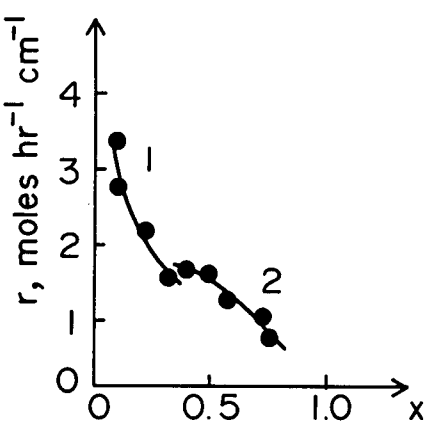

Fig. 7. Conversion curves of toluene hydrogenation reaction at $T = 216$°C[14]:

1, $\rho = 3.3$ and $\delta = 1.2$;
2, $\rho = 14.5$ and $\delta = 5.3$.

(with a reversibility correction for the main route) are represented by curve 1 in Figs. 1 and 2, respectively, characterizing the conditions: $h_1=h_2>0$ and $\sum_j n_{1j} \geqslant l_1$. It can be seen from the curves in Fig. 6 that the reaction rates are inhibited by the desirable product (isoprene). The results obtained enabled us to establish a kinetic model of this process including an equation of isoprene formation rate

$$r_1 = \frac{k_1 P_{C_5H_{10}} \gamma}{c^{2/3} + k_3 P_{C_5H_8}} \tag{27}$$

and an equation of cracking by-product formation rate

$$r_2 = \frac{k_2 P_{C_5H_{10}}}{c^{2/3} + k_3 P_{C_5H_8}}, \tag{28}$$

where c is the amount of coke deposited on the catalyst.

Kinetic equation of coke formation and catalyst regeneration were also obtained.

Hydrogenation of toluene over a nickel catalyst.

The reaction occurs within a temperature range of 150 to 270°C with a high selectivity[14] and is characterized by a single route described by the following stoichiometric equation:

$$C_7H_8 + 3H_2 = C_7H_{14}. \tag{29}$$

The experimental results of the reaction rate as a function of temperature with a reversibility correction (γ) are linearized in coordinates similar to Arrhenius' coordinates and described by straight line 6 in Fig. 1. The kinetic equation is, therefore, a power equation with a formally negative activation energy value. The reaction rate as a function of dilution is represented by curve 1 in Fig. 2 characterized by the condition $\sum_j n_j > 0$. The optimum reaction rate for the initial composition of the reaction mixture (curve 3e in Fig. 3), which is close to stoichiometric, defines the condition $\sum_j n_j > n_2$. Here the dependences of reaction rates on conversion are characterized by concave conversion curves (cf. curve 1 in Fig. 7) which indicates high-order reaction rates for the concentrations of reacting components and points to the fact that the kinetics of the process is described by the following equation:[14]

$$r = k P_{C_7H_8}^{0.5} P_{H_2}^{3} \gamma, \tag{30}$$

which satisfies condition (24) for concavity of the $r(x)$ functions. If the

hydrogen/toluene ratio is higher than stoichiometric, the experimental dependence of reaction rate on reaction mixture compositions fail to pass through a maximum and corresponds to curve 2d in Fig. 3 characterized by the condition $\sum_j n_j > 0$. The conversion curves are convex (cf. curve 2 in Fig. 7), that is characteristic of a slight dependence of reaction rate on the concentration of initial components. The character of these curves corresponds to a kinetic equation

$$r = k' P^{0.5}_{C_7H_8} \gamma , \tag{31}$$

which satisfies condition (24) for the convexity of the $r(x)$ functions in the above variation range of the process parameters.

It can be seen that we have here is a transition of the conversion curves from one shape to another due to a change in the initial component ratio. Eq. (30) is a general equation for reaction (29) and, in particular case, can transform to (31) at greater ρ.

Hydrogenolysis of n-pentane over platinum and nickel.[15]

It was seen from the investigation of this process in the presence of platinum and excess hydrogen at 420～480°C that a variation of reaction conditions tends to change initial selectivity extrapolated to $x=0$. This suggests a parallel reaction scheme:

$$n\text{-}C_5H_{12} = i\text{-}C_5H_{12} , \tag{32}$$

$$2n\text{-}C_5H_{12} + 2H_2 = CH_4 + C_2H_6 + C_3H_8 + C_4H_{10} . \tag{33}$$

The process selectivity varies inversely with conversion and is described by curve 3c in Fig. 5 characterized by the conditions $\sum_j n_{1j} < \sum_j n_{2j}$ at $l_1 \leqslant l_2$ or $\sum_j n_{1j} > \sum_j n_{2j}$ at $l_1 \ll l_2$. Selectivity as a function of nitrogen dilution and hydrogen-to-*n*-pentane ratio is represented by curves 1′ and 2″ in Fig. 4, respectively. The curves are characterized by the conditions $\sum_j n_{1j} - l_1 > \sum_j n_{2j} - l_2$ and $\sum_j n_{1j} - n_{12} < \sum_j n_{2j} - n_{22}$ at $\sum_j n_{1j} - l_1 > \sum_j n_{2j} - l_2$, respectively. Temperature dependence of selectivity is described by curve 1 in Fig. 4 for the condition $E_1 - E_2 < (H)_{T_{min}}$.

Temperature dependences of reaction rates for the main and the side route are represented by curves 2 and 1 in Fig. 1, respectively, which correspond to the conditions $l_1=0$ and $h_2>0$. These conditions indicate that the kinetic equation has a power form for the first route and other than power form for the second route. The reaction rate for the main route as a function of nitrogen dilution and reaction mixture composition corresponds

to curves 1 and 3e in Figs. 2 and 3, respectively, characterized by the conditions $\sum_j n_{1j}>0$ and $\sum_j n_{1j}>n_{22}$. Reaction rate for the side route as a function of δ and ρ is represented by curves 3 and 1b in Figs. 2 and 3, respectively, which indicate the condition $\sum_j n_{2j}=l_2$. Kinetic equations for isopentane formation rate

$$r_1=k_1P_{C_5H_{12}}P_{H_2}^{0.5} \tag{34}$$

and hydrogenolysis product formation rate

$$r_2=\frac{k_2P_{C_5H_{12}}}{P_{H_2}+k_3P_{C_5H_{12}}} \tag{35}$$

can be derived from this analysis.

An investigation of the same process over nickel in a temperature range of 230 to 270°C showed that the reaction only proceeds in the direction of hydrogenolysis products. Experimental dependences of reaction rate on temperature and reaction mixture dilution correspond to curves 1 and 3 in Figs. 1 and 2, respectively, characterized by the conditions $h>0$ and $\sum_j n_j=1$. This has offered a possibility of describing experimental data by Eq. (35).

Some other analyses of selectivities and reaction rates as a function of reaction conditions and conversion which were aimed at elucidating process schèmes and the form of kinetic equations are discussed in our papers[1~6].

Conclusion

It is shown that the analysis of reaction rate and selectivity changes with varying process conditions can be effectively employed for elucidating the form of kinetic models. The results of these analyses will appreciably aid in selecting kinetic models for calculating experimental data by electronic computers.

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