Physical Chemistry

A. P. Rudenko

1964

SovietRxiv

Abstract

Full Text

Physical Chemistry

A. P. Rudenko

Self-Developing Catalytic Systems

(Presented by Academician A. A. Balandin, 23 VI 1964)

If conditions are created for the continuous course of some catalytic reaction that does not proceed without a catalyst or is strongly accelerated by a catalyst, with ideal exchange of matter and energy with respect to the catalyst and with other constant conditions (temperature, pressure or volume, etc.), then an open stationary system is formed

$$\mathrm{A}+\mathrm{B}+\cdots \longrightarrow \left|\frac{\mathrm{A}+\mathrm{B}+\cdots \rightarrow \mathrm{C}+\mathrm{D}+\cdots+(-\mathrm{dF},\,-\mathrm{dZ})}{\mathrm{K}}\right| \xrightarrow{\mathrm{C}+\mathrm{D}+\cdots+(-\mathrm{dF},\,-\mathrm{dZ})} \tag{1}$$

Let us represent, within the sphere of existence of such a system, an elementary catalytic system as the aggregate of the catalysis center with the components and products of the reaction at all stages of the catalytic act. The preservation of the basic constant conditions of the course of this reaction, which we shall call the basic reaction, over a time t maintains the dynamic existence of the catalytic system and preserves unchanged the nature of the catalysis center over the time t. The catalysis center may be an elementary unit of a heterogeneous or homogeneous catalyst possessing all its catalytic properties and consisting of the aggregate of its atoms that directly interact with the reaction components (the functional group of the center), together with all the other atoms or molecules of the catalyst that are bound to the functional group and influence its manifested catalytic properties. To a definite nature of the catalysis center (its composition and structure) under the indicated conditions there will correspond a strictly definite catalytic activity, which in this case is a constant quantity and is measured by the productivity of the catalysis center $a = n/t$, where n is the number of catalytic acts occurring during time t. As a result of microfluctuations of the conditions and normal errors, including the appearance in the reaction sphere of any foreign substances (which constitute a variable complex of auxiliary conditions unable to terminate the course of the basic reaction), various random changes in the nature of the catalysis centers and in the stationarity of the system become possible. Among such successive multiple changes in the nature of the catalysis center,

$$\mathrm{K}_0 \rightarrow \mathrm{K}_1 \rightarrow \mathrm{K}_2 \rightarrow \cdots \rightarrow \mathrm{K}_q \tag{2}$$

Fig. 1

Figure 1: Fig. 1

there may be its crystal-structural, adsorption-physical, and chemical transformations.

The probability of preserving the initial catalytic activity of the catalysis center upon a single change in its nature $\mathrm{K}_i \to \mathrm{K}_{i+1}$ must be negligibly small in comparison with the probabilities of an increase or decrease in catalytic activity, and the latter events must be equally possible, with probabilities close to 0.5. Passing to mean values, it can be shown that the following statistical law of change in absolute catalytic activity holds, together with its corresponding scheme (Fig. 1),

$$\overline{a_i} = a_0 \overline{k_g^j}, \tag{3}$$

where $\overline{a_i}$ is the mean value of the absolute catalytic activity from all its possible random values upon increase or decrease in each-

variant of stage $i = q{-}1,\ i = 0, 1, 2, 3, \dots, (q{-}1)$; a_0 is the catalytic activity of the initial catalytic center K_0, in the scheme $a_0 = 1$; $\bar{k}_g$ is the mean geometric value of the development coefficient, $\bar{k}_g > 1$; $j = \log_{\bar{k}g} \bar{a}_i,\ \ j = 0, \pm 1, \pm 2, \dots, \pm(q-1)$.

The scheme describes the development of catalytic systems with respect to the principal catalytic property, the absolute catalytic activity in one and the same base reaction.

With development up to stage q one has

$$\Omega_q = \omega_{q1},\ \omega_{q2}, \dots$$

$$\dots, \omega_{q\,2^{q-1}} = 2^{q-1} \tag{4}$$

different paths. Each path is uniquely described by a set of indices j (levels of development) traversed by the corresponding selective trajectory $\omega_{q\varepsilon}$ at each of the stages $1, 2, 3, \dots, (q-1)$. Each such set of indices j can be represented as a particular value of the evolutionary function describing any path of development of catalytic systems

Fig. 1

$$^{[1]}[\varepsilon_q, F(j,q)] = J(\omega_{q\varepsilon}, j_{\gamma\delta}) = J(\omega_{q\varepsilon}, j) = J \tag{5}$$

$$\varepsilon = 1, 2, \dots, 2^{q-1}; \qquad \gamma, \delta = 1, 2, \dots, q; \qquad \gamma \leqslant \delta.$$

Considering the probability variables of Markov random processes described by the evolutionary function along each path of development of catalytic systems $J(\omega_{q\varepsilon}, j)$, and comparing the course of their changes and the values attained at each stage of development with the course of changes and values of other evolutionary characteristics of catalytic systems, we find the following.

With the greatest probability

$$P(J(\omega_{q\varepsilon}, j)) = \left(\frac{a_0 t\bar{p}}{2(1-\bar{p})}\right)^q \cdot \bar{k}_g^{\Sigma(J)} \cdot (1-\bar{p})^{tA(J)}, \tag{6}$$

(where $\bar{p}$ is the mean elementary probability in the space of all random processes $J(\omega_{q\varepsilon}, j)$) there develops that path $J(\omega_{q\varepsilon}, j)$ up to stage q for which the sum A of the catalytic activities of the catalytic centers in the genetic series (2) is greatest; the energy Q released by the base catalytic reaction is greatest; the measure of progressiveness of development Ψ is greatest; the rate V of realization of the path is greatest; the selectivity of natural selection of catalytic centers and the catalytic systems associated with them is greatest, etc.:

$$A(J(\omega_{q\varepsilon}, j)) = a_0 \sum_{(J)} \bar{k}_g^j, \tag{7}$$

$$Q(J(\omega_{q\varepsilon}, j)) = \left(\frac{-\partial F,\ -dZ}{N_A}\right) a_0 t \sum_{(J)} \bar{k}_g^j \tag{8}$$

(N_A is Avogadro' s number),

$$\Psi(J(\omega_{q\varepsilon}, j)) = \bar{k}_g^{\Sigma(J(\omega_{q\varepsilon}, j))}, \tag{9}$$

$$V(J(\omega_{q\varepsilon}, j)) = \frac{a_0}{n} \sum_{(J)} \bar{k}_g^j. \tag{10}$$

$$\mathrm{Sel}(J(\omega_{q\varepsilon}, j)) = \bar{k}_g^{\Sigma(J)} : \sum_{\varepsilon=1}^{2^{q-1}} \bar{k}_g^{\Sigma(J)}. \tag{11}$$

Maximum values are also attained in this case by a number of other evolutionary characteristics (the total and average rate of energy release of the base reaction, the degree of development, the degree of organization of catalytic systems, etc.). All of them are functional dependences of the physical characteristics of the development of catalytic systems on the principal variable j, whose law of change is specified by the particular value of the evolutionary function J for the given path of development $J(\omega_{q\varepsilon}, j)$. Only the total time required for carrying out the given path of development has a minimum value

$$T(J(\omega_{q\varepsilon}, j)) = \sum_{(J)} t_{ij} = \frac{n}{a_0} \sum_{(J)} \frac{1}{\bar{k}_g^j}. \tag{12}$$

Consequently, in the spontaneous process of changes in the nature of the catalytic centers (2), on the basis of the continuously proceeding catalytic reaction (1),

Table 1

$j_{\gamma 5} = \log_{\bar{k}g} a_4$	$J(\omega_{5\varepsilon}, j)$	$\sum_{q=1}^{5}(J(\omega_{q\varepsilon}, j))$	$\bar{k}_g = 1.2$; $\sum_{\varepsilon=1}^{16} \bar{k}_g \exp \sum J(\omega_{5\varepsilon}, j) =$ 25.553 − $\Psi(J)$	$\bar{k}_g = 1.2$; $\sum_{\varepsilon=1}^{16} \bar{k}_g \exp \sum J(\omega_{5\varepsilon}, j) =$ 25.553 − $\mathrm{Sel}(J), \%$	$\bar{k}_g = 2$; $\sum_{\varepsilon=1}^{16} \bar{k}_g \exp \sum J(\omega_{5\varepsilon}, j) =$ 1386.65 $-\Psi(J)$	$\bar{k}_g = 2$; $\sum_{\varepsilon=1}^{16} \bar{k}_g \exp \sum J(\omega_{5\varepsilon}, j) =$ 1386.65 − $\mathrm{Sel}(J), \%$
+4	$0 + 1 + 2 + 3 + 4$	+10	6.18	24.185	1024	74.047
+2	$0 + 1 + 2 + 3 + 2$	+8	4.29	16.788	256	18.461
+2	$0 + 1 + 2 + 1 + 2$	+6	2.98	11.662	64	4.615
+2	$0 + 1 \quad 0 + 1 + 2$	+4	2.07	8.100	16	1.153
+2	$0 - 1 \quad 0 + 1 + 2$	+2	1.44	5.635	4	0.288
0	$0 + 1 + 2 + 1 \quad 0$	+4	2.07	8.100	16	0.153
0	$0 + 1 \quad 0 + 1 \quad 0$	+2	1.44	5.635	4	0.288
0	$0 - 1 \quad 0 + 1 \quad 0$	0	1.00	3.913	1	0.072
0	$0 + 1 \quad 0 - 1 \quad 0$	0	1.00	3.913	1	0.072

$j_{\gamma 5} = \log_{\bar{k}g} a_4$	$J(\omega_{5\varepsilon}, j)$	$\sum_{q=1}^{5} (J(\omega_{q\varepsilon}, j))$	$\bar{k}_g = 1.2$; $\sum_{\varepsilon=1}^{16} \bar{k}_g \exp \sum J(\omega_{5\varepsilon}, j) =$ 25.553 – $\Psi(J)$	$\bar{k}_g = 1.2$; $\sum_{\varepsilon=1}^{16} \bar{k}_g \exp \sum J(\omega_{5\varepsilon}, j) =$ 25.553 – Sel(J), %	$\bar{k}_g = 2$; $\sum_{\varepsilon=1}^{16} \bar{k}_g \exp \sum J(\omega_{5\varepsilon}, j) =$ 1386.65 $-\Psi(J)$	$\bar{k}_g = 2$; $\sum_{\varepsilon=1}^{16} \bar{k}_g \exp \sum J(\omega_{5\varepsilon}, j) =$ 1386.65 – Sel(J), %
0	$0 - 1 \quad 0 - 1 \quad 0$	−2	0.694	2.715	0.25	0.01802
0	$0 - 1 - 2 - 1 \quad 0$	−4	0.483	1.890	0.0625	0.00451
−2	$0 + 1 \quad 0 - 1 - 2$	−2	0.694	2.715	0.25	0.01802
−2	$0 - 1 \quad 0 - 1 - 2$	−4	0.483	1.890	0.0625	0.00451
−2	$0 - 1 - 2 - 1 - 2$	−6	0.335	1.311	0.0156	0.00113
−2	$0 - 1 - 2 - 3 - 2$	−8	0.233	0.911	0.0039	0.00028
−4	$0 - 1 - 2 - 3 - 4$	−10	0.161	0.630	0.0009	0.00007

provided certain conditions are observed, the principle is realized of the greatest probability of such successive, repeated changes in the nature of the catalytic centers and of the catalytic systems associated with them, which lead to a successive increase, or to the greatest increase, in the catalytic activity, the amount and rate of energy release of the base reaction, and to the greatest increase in other evolutionary characteristics. This principle of the greatest probability of the realization of the most progressive paths of development of catalytic systems, characterized by the greatest accumulation of certain positive traits, is a stable regularity of probabilistic type, with stability determined by

$$\mathcal{E}(q, \bar{k}_g, \bar{f}) = \sum_{i=0}^{q} \sum_{\varepsilon=1}^{2^i} \left(\frac{-dF, -dZ}{N_A} \right) a_0 t \sum_{(J)} \bar{k}_g^j. \tag{13}$$

The indicated regularity must manifest itself whenever conditions are created for the self-development of catalytic systems, and it has the significance of the fundamental law of their evolution. From (13) it is seen that the stability (inevitability of manifestation) of the fundamental law of evolution of catalytic systems is the greater, the

the more stages of development q have been carried out, the larger the development coefficient $\bar{k}_q$, and the greater the isothermal potential of the basic catalytic reaction at constant volume or pressure

$$\left(\frac{-dF, -dZ}{N_A}\right).$$

The latter circumstance also explains the preference for energy-rich exothermic reactions when choosing them as the basic catalytic reaction.

To illustrate the operation of the basic law of evolution of catalytic systems and to explain the formulas and scheme in Table 1, the results are given of calculating the selectivity of natural selection of catalysis centers in the self-development of catalytic systems along all possible paths up to 5 stages, in two cases: $\bar{k}_g = 1.2$ and $\bar{k}_g = 2$.

The basic law of evolution of catalytic systems is revealed theoretically under two assumptions corresponding to nonideal catalytic phenomena. Namely, 1) it is necessary that the elementary probability of a change in the nature of a catalysis center be greater than zero, and 2) there must exist some variable complex of random conditions that ensures any random transformations of the catalyst, distinct from its cyclic transformations in catalytic acts.

The majority of known real catalytic processes (especially in the field of heterogeneous catalysis) may be assigned to such nonideal catalytic phenomena, in which changes in the catalysts and in their catalytic activity during the process are the rule rather than the exception. Various changes are known in the catalytic activity of nonstationary heterogeneous catalysts, proceeding both toward its increase and toward its decrease, or along a more complex path. For example, the fact of the development of chromium catalysts in dehydrogenation processes and many others is well known. A number of works may be cited ([1–9] and others) in which attention is drawn to changes in catalysts during the reaction.

Consequently, the study of the evolutionary regularities of catalytic processes will constitute a new field of catalytic chemistry—evolutionary catalysis, in which the variable nature of the catalyst is recognized and its random changes are studied in the form in which they actually occur in real catalytic phenomena, as well as certain special catalytic processes carried out under conditions ensuring strongly expressed directed changes of catalysts.

Moscow State University
named after M. V. Lomonosov

Received
23 VI 1964

CITED LITERATURE

1. G. K. Boreskov, *ZhFKh*, **32**, 2739 (1958); **33**, 1969 (1959).

2. A. A. Balandin, *Scientific Notes of Moscow University*, no. 175, Dept. of Chemistry, 110 (1956).

3. A. B. Shekhter, I. I. Tretyakov, in: *Heterogeneous Catalysis in the Chemical Industry*, Moscow, 1955, p. 349.

4. A. Guotmi, R. Cunningham, in: *Catalysis. Studies of the Surface of Catalysts*, IL, 1960, p. 74.

5. V. M. Gryaznov, Doctoral dissertation, Moscow, 1962.

6. A. P. Rudenko, *Bulletin of Moscow University*, Chemistry series, no. 2, 59 (1961).

7. A. A. Balandin, A. P. Rudenko, G. S. Tener, *Proceedings of the USSR Academy of Sciences, Department of Chemical Sciences*, 1961, 763.

8. B. P. Bruns, *DAN*, **78**, 79 (1951); Dissertation, Moscow, 1955.

9. V. A. Komarov, N. S. Burevova, *Scientific Notes of Leningrad University*, no. 211, 188 (1957).

Note: Figure translations are in progress. See original paper for figures.