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STUDIES OF DYNAMIC PROPERTIES OF HETEROGENEOUS CATALYTIC REACTIONS IN A CLOSED ISOTHERMAL GRADIENTLESS SYSTEM OVER BIOGRAPHICALLY INHOMOGENEOUS CATALYST SURFACE

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The dynamics of a closed isothermal system of constant volume consisting of an ideal gaseous mixture and particles adsorbed over the biographically inhomogeneous catalyst surface, has been studied. The existence, uniqueness and asymptotic stability of the point of detailed equilibrium in each positive reaction simplex has been proved.

Исследована динамика замкнутой изотермической системы постоянного объёма, состоящей из идеальной газовой смеси и частиц, адсорбированных на биографически неоднородной поверхности катализатора. В частности, доказано существование, единственность и асимптотическая устойчивость точки детального равновесия в каждом положительном реакционном симплексе.

Dynamic properties of closed systems have been studied by several authors /1–6/. If the axioms formulated in Ref. /1/ are valid, the free energy of the system is a Lyapunov function for the respective system of differential equations. This axiomatics is satisfied by the kinetics of the mass action law (MAL), i.e. the point of detailed equilibrium (PDE) for an ideal homogeneous system is asymptotically stable in the reaction simplex. The most complete and strictest study of the dynamics of closed systems with MAL was carried out by Vasiliev et al. /2/. In contrast to Ref. /1/, they had constructed their arguments so that the results are valid not only for ideal homogeneous but also for ideal heterogeneous systems. In Ref. /3/ for the MAL kinetics, the PDE is shown to be the stable node on the invariant plane.

At the same time, of great interest are the nonideal systems wherein the MAL is unapplicable. Akramov et al. /4/ considered some systems for which the Marselen-de

Donde kinetics (MDD) /7/ holds and proved properties for it which are similar to those of MAL kinetics. In Ref. /5/ it was proved that the PDE is the stable node for these systems and in Ref. /6/ closed systems with MAL kinetics were described, wherein diffusion is possible.

The results of Refs. /8–12/ indicate that the MAL kinetics cannot be applied for the description of heterogeneous catalytic reactions over a biographically inhomogeneous catalyst surface. Let us analyze these results. Let a series of elementary reactions proceed in the system, which are of the type (σ takes values s and –s)

$$\sum_{i=1}^{N} b\beta_i\ {}_i + \sum_{l=1}^{M} \beta_{\gamma_l} ZI_l + \left(m_{t_s} - \sum_{l=1}^{M} \beta_{\gamma l} \right) Z = TS \rightarrow \text{products} \qquad (1)$$

where β_i are gaseous substances; ZI is the adsorbed particle; Z is a vacant site of the surface; TS is the activated complex; m_{t_s} is the number of surface sites occupied by the activated complex; $b_{\gamma i}$ and $\beta_{\gamma l}$ are the stoichiometric coefficients; N is the number of gaseous substances and M is the number of adsorbed particles. The rate of reaction (1) in /8–9/ was described as

$$U_\gamma = \kappa_s \frac{kT}{h} \exp\left(- \frac{\mu_s^\ddagger}{kT} \right) \exp\left(\frac{\sum_{i=1}^{N} b_{\gamma i} \mu B_i + \sum_{l=1}^{M} \beta_{\beta l} \mu_{al}}{kT} \right) \qquad (2)$$

Here κ_l is the transmission coefficient, k and h are the Boltzmann and Planck constants, $\mu_\gamma^\ddagger$ is the chemical potential of the reaction σ minus kTln C ($C_\gamma^\ddagger$ is the concentration of the activated complexes), μ_{B_i} and μ_{a_l} are the chemical potentials of gaseous and adsorbed substances. According to Ref. /10/,

$$\mu_{a_l} = -kT\ln j_{a_l} + kT\ln \frac{Z_l}{Z_{oc}} - kT\ln U \qquad (3)$$

where j_{a_l} is the internal statistical sum of adsorbed particle,

$$Z_{oc} = \sum_{e=1}^{M} Z_l$$

is the portion of the occupied surface, the parameter U is a function of Z_{oc} and is determined from the equation

$$Z_{oc} = \frac{\gamma}{\exp(\gamma f) - 1} \int_0^f \frac{\exp[-(1-\gamma)\lambda]}{U + \exp(-\lambda)} d\lambda \qquad (4)$$

where γ is the parameter of the distribution function, f is the maximum value of the relative desorbability index λ. According to Ref. /11/, since $\mu_\gamma^\ddagger$ for the forward ($\sigma = s$) and reverse ($\sigma = -s$) directions of the same step coincide

$$\mu_s^\ddagger = \mu_s^0 - m_{t_s} kT\ln I(\alpha_s - \gamma, U, f) \qquad (5)$$

where

$$I(\alpha_s - \gamma, U, f) = \int_0^f \frac{\exp[-(\alpha_s - \gamma)\lambda}{1 + U^{-1}\exp(-\lambda)} d\lambda \qquad (6)$$

Here α_s is the transfer coefficient. From eqs. (4)–(6) it is clear that $\mu_s^\ddagger$ is independent of Z_{oc}.

The kinetics of practical reactions are often described by using the approximation of mean coverages. In this case the chemical potentials are described by the equations /12/

$$\gamma = 0 \quad \mu_{a_1} = \mu_{a_1}^0 + kT\ln Z_1 + \Delta q \cdot Z_{oc} - kT\ln Z_{oc} \qquad (7)$$

$$\gamma < 0 \quad \mu_{a_1} = \mu_{a_1}^0 + kT\ln Z_1 + \frac{kT}{\gamma} \ln Z_{oc} - kT\ln Z_{oc} \qquad (8)$$

$$\gamma < 0 \quad \mu_{a_1} = \mu_{a_1}^0 + kT\ln Z_1 + \frac{kT}{\gamma} \ln(1 - Z_{oc}) - kT\ln Z_{oc} \qquad (9)$$

The system of differential equations describing variations in the concentrations of gaseous substances and the coverages with the time is

$$\frac{dc}{dt} = S_k B_1^T u \tag{10}$$

$$L \frac{dZ}{dt} = S_k B_2^T u \tag{11}$$

where c is the vector of gas concentrations, Z is the coverage vector, u is the vector of the rates of steps, L is the number of catalytic centers per unit reactor volume, S_k is the area of the catalyst surface per unit reactor volume and B_1 and B_2 are the submatrices of the stoichiometric matrix referring to the gaseous substances and coverages, respectively.

Let R^+_{N+M} and R^+_{N+M} be the negative and positive constants of the reaction space. Introduce the matrix $B = (B_1, B_2/L)$. The reaction space L_R is a linear envelope stretched over the matrix B rows. Let C_0 be a nonnegative vector of the initial data for all concentrations. The set

$$L_S = (L_R + C_0) \cap R^+_{N+M}, \sum_{i=1}^{M} Z_i < 1 \tag{12}$$

will be referred to as a positive reaction simplex.

As is seen from eqs. (2)–(9), the kinetics under consideration differs from the MAL kinetics in the fact that the vacant site of the catalyst surface does not enter into the number of intermediates, and the rate "constants" of elementary reactions depend on the coverages. It can easily be proved that even for ideal heterogeneous catalytic reactions eq. (2) does not reduce to MAL kinetics.

For problem (10)–(11) *the following statements* are valid.

1. Matrix $A = [\![\delta\mu_i(c)/\delta c_j]\!]$ is positively determined in R^+_{N+M}. It holds for the chemical potentials determined by any of the eqs. (3), (7)–(9).

2. The solution for eqs. (10)–(11) does exist at all $t \in [0, \infty]$. For nonnegative and positive initial data it will be nonnegative and positive, respectively. The same is also valid for the portion of vacant surface sites of the catalyst $Z_0 = 1 - Z_{oc}$.

3. In each positive reaction simplex L_S, PDE always exists and is unique. All nonnegative points in eqs. (10)–(11) are the PDE.

4. The positive PDE is stable in R^+_{N+M} and asymptotically stable in L_S.

5. The set of ω-limiting points in eqs. (10)–(11) consists of PDE. If on the boundary of L_S (there are no stationary points, any trajectory beginning in L_S) will converge to the positive PDE. There exists no nonnegative periodic solution.

6. In the positive PDE, the matrix of a linear approximation for eqs. (10)–(11) has nonpositive eigenvalues. If a part of the concentration is expressed through the laws of conservation and the system (10)–(11) is considered in a shortened form, the eigenvalues are negative, i.e. the positive PDE is a stable node in L_S.

For catalytic systems it is a common practice to consider only system (11) relative to the coverages, assuming the gas concentrations to be constant. The PDE for such a system will be referred to as a vector of coverages at which the rates of all reaction steps are equal to zero. Then, if one assumes that there exists at least one positive PDE, statements 3–6 are valid.

The dynamics of a closed adiabatic system will be described elsewhere.

REFERENCES

1. F. J. Krambeck: Arch. Rat. Mech. Anal., *38*, 317 (1970).
2. V. M. Vasiliev, A. I. Volpert, S. I. Khudyaev: Zh. Vychisl. Mat. Matem. Fiz., *13*, 683 (1973).
3. T. A. Akramov, G. S. Yablonskii: Zh. Fiz. Khim., *49*, 1818 (1975).
4. T. A. Akramov, V. I. Bykov, G. S. Yablonskii: in Mathematical Problems of Chemistry, Part I, p. 206. Computing Center, Novosibirsk 1975.
5. V. I. Bykov, A. N. Gorban, V. I. Dimitrov: React. Kinet. Catal. Lett., *12*, 19 (1979).
6. T. A. Akramov: Dokl. Akad. Nauk SSSR, *244*, 554 (1979).
7. M. Feinberg: Arch. Rat. Mech. Anal., *46*, 1 (1972).
8. Yu. S. Snagovskii: Kinet. Katal., *21*, 189 (1980).
9. F. S. Shub, A. G. Zyskin, M. G. Slinko, M. I. Temkin: Kinet. Katal., *21*, 396 (1980).
10. Yu. S. Snagovskii: Kinet. Katal., *19*, 932 (1978).
11. Yu. S. Snagovskii: Kinet. Katal., *17*, 92 (1976).
12. Yu. S. Snagovskii: Kinet. Katal., *16*, 1435 (1975).