

## SOME RELATIONS BETWEEN THERMODYNAMIC AND KINETIC PARAMETERS IN HETEROGENEOUS CATALYSIS

NGUYEN XUAN QUANG<sup>a</sup>, HO SI THOANG<sup>b</sup> and Milan ŠÍPEK<sup>c</sup>

<sup>a</sup> *Institute of Chemical Process Fundamentals,*

*Czechoslovak Academy of Sciences, 165 02 Prague 6, Czechoslovakia*

<sup>b</sup> *Institute of Chemistry, National Centre for Scientific Research,*

*Nghia-do Tu-liem, Hanoi, Vietnam and*

<sup>c</sup> *Department of Physical Chemistry,*

*Prague Institute of Chemical Technology, 166 28 Prague 6, Czechoslovakia*

Received January 16, 1989

Accepted February 28, 1989

*Dedicated to late Academician Eduard Hála.*

---

The results of our preceding work on irreversible (rational) thermodynamics of reacting mixture of fluids and a solid substance are applied to the problem of heterogeneous catalysis. The negative effect of diffusion and the positive effect of surface forces are justified, and the Brønsted–Polanyi equation for the activation energy of surface reaction is obtained.

---

The finding of relationships between thermodynamic and kinetic parameters of diffusion, adsorption, and chemical surface reaction<sup>1,2</sup> pertains to the main problems of heterogeneous catalysis. Many experimental results have not been hitherto fully accounted for, such as, e.g., the negative effect of diffusion on the chemical surface reaction or the empirical Brønsted–Polanyi equation for the activation energy of surface reaction. Here we shall show that these results are to be achieved within the framework of the phenomenological, irreversible (rational) thermodynamics of a chemically reacting mixture of fluids and a solid<sup>3</sup>. It is assumed that this three-dimensional model of thermodynamics of continuum is able to model the behaviour of chemically reacting gases or liquids around the catalyst surface.

Vector  $\mathbf{k}_\alpha$  in the momentum balance of a mixture component (Eq. (23) in ref.<sup>3</sup>) has the physical meaning of interaction volume force acting on the mixture component  $\alpha$  which originates in the other mixture components. Thus, quantity  $\mathbf{F}$  defined by

$$\mathbf{F} = \sum_{\alpha=1}^n \mathbf{k}_\alpha \quad (1)$$

$n$  is the number of mixture components; thereto the  $n$ -th component is the solid —

catalyst, and the others are fluids, i.e., gases or liquids) can be interpreted as the overall interaction force in the catalyst surface layer. Let us remark that it is possible to write  $\mathbf{F}$  also in terms of quantities  $\mathbf{p}_\alpha$

$$\mathbf{F} = \sum_{\alpha=1}^n \mathbf{p}_\alpha \quad (2)$$

occurring in the resulting relation for the entropy production, Eq. (70) in the preceding work<sup>3</sup>, if we employ definition (74) in ref.<sup>3</sup>, and  $\mathbf{p}_n$  is suitably defined up. Quantity  $\mathbf{F}$  is connected, by means of the momentum balance of mixture (Eq. (24) in ref.<sup>3</sup>), with reaction rates of conversions of fluid components  $r_\beta$  ( $\beta = 1, \dots, n-1$ ) of chemical (surface) reactions and with diffusion expressed by the diffusion velocities of fluid components  $\mathbf{u}_\beta$  (i.e., the relative velocities of fluid components towards the catalyst); see Eqs (8), (24), (20), and (22) in ref.<sup>3</sup>:

$$\mathbf{F} = - \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta = - \sum_p \left( \sum_{\beta=1}^{n-1} \varrho_\beta^{-1} P^{p\beta} M_\beta \mathbf{J}_\beta \right) J_p. \quad (3)$$

The first sum is taken over all independent chemical reactions  $p$  with rates  $J_p$  (for their relation to  $r_\beta$  see Eqs (35) and (34) in ref.<sup>3</sup>) where the fluid components  $\beta = 1, \dots, n-1$  have their stoichiometric coefficients  $P^{p\beta}$  (in  $p$ -th reaction) and molar masses  $M_\beta$ ;  $\mathbf{J}_\beta$  are diffusion flows defined by

$$\mathbf{J}_\beta = \varrho_\beta \mathbf{u}_\beta, \quad \beta = 1, \dots, n-1. \quad (4)$$

In Eqs (3) and (4),  $\varrho_\beta$  is the density of component  $\beta$  (mass concentration). Let us remark that, owing to  $\mathbf{J}_n = \mathbf{0}$ , it is possible to replace the sum from  $\beta = 1$  to  $n-1$  in Eq. (3) by the sum from  $\alpha = 1$  to  $n$  with non-zero  $P^{pn}$ ; thus, the catalyst may generally take part in chemical reactions but in such a way that the resulting rate of its conversion is zero,  $r_n = 0$  (from Eq. (35) in ref.<sup>3</sup>,  $\sum_p J_p P^{pn} = 0$  holds for the catalyst).

Since in our phenomenological model,  $\mathbf{F}$  represents the overall interaction force in the surface layer of catalyst, it can be identified, from the molecular point of view, with the surface electrostatic forces and with the surface bond forces. For the given system catalyst-reactants, this force is therefore to be considered, at least in the first approximation, as constant (e.g., independent of transport in the vicinity of surface). Therefore it is possible to judge from Eq. (3) that the increase in reaction rates can be achieved by reducing the diffusion flows  $\mathbf{J}_\beta$ , and consequently the diffusion processes play negative role in catalytic reactions.

It follows also from Eq. (3) that the greater surface forces, the more rapid is the reaction (at constant diffusion). This is in agreement with the common interpretation according to which the adsorption (which is greater at greater  $\mathbf{F}$ ) is a reversible

process of the formation of activated complexes. If  $F$  is small, the activated complexes are less stable, consequently they are fewer, and the reaction takes place slower.

Let us define the adsorption (surface) energy  $\Delta E$  as the energy needed to overcome surface force  $F$  from the homogeneous phase (from infinity) to the distance  $r_0$  of adsorbed complex

$$\Delta E = \int_{\infty}^{r_0} F \cdot dr, \quad (5)$$

where we integrate along coordinate  $r$ . If we limit ourselves to the only independent reaction (with rate  $J$  and stoichiometric coefficients  $P^\beta$ ), we get with respect to the validity of Eq. (3)

$$\Delta E = \int_{r_0}^{\infty} \left( J \sum_{\beta=1}^{n-1} \varrho_\beta^{-1} M_\beta P^\beta J_\beta \right) \cdot dr. \quad (6)$$

For  $J$  (or for the reaction rate constant) we assume the validity of the Arrhenius equation

$$J = [A \exp(-E_a/RT)] f(\varrho_1, \dots, \varrho_n), \quad (7)$$

where  $E_a$  is the activation energy of (surface) reaction,  $R$  the gas constant,  $T$  the thermodynamic temperature,  $A$  the frequency factor, and  $f(\varrho_1, \dots, \varrho_n)$  is the concentration dependence of reaction rate. For the diffusion we assume the Fick law to apply with the Arrhenius form of the dependence of diffusion coefficient on temperature:

$$J_\beta = - \sum_{\delta=1}^{n-1} D_{\beta\delta} \exp(-E_{\delta\beta}/RT) \text{grad } \varrho_\delta, \quad \beta = 1, \dots, n-1. \quad (8)$$

On the assumption of the approximate equality of the diffusion activation energy for all the components  $E_{\delta\beta} \approx E_D$  and their independence of coordinate  $r$ , on inserting Eqs (7) and (8) into (6), one can obtain

$$\Delta E = K \exp[-(E_a + E_D)/RT], \quad (9)$$

where  $K$  is a function of concentrations. If this assumption is not met, the diffusion activation energy differs from  $E_D$  by the value of  $\varepsilon_{\delta\beta}$ . Then  $K$  is a function not only of concentration but also of temperature. Since values  $E_D$  and  $E_a$  of surface reaction in heterogeneous catalysis are relatively small, Eq. (9) may be approximated by the relation

$$\Delta E = K[1 - (E_a + E_D)/RT], \quad (10)$$

which can be written in the form

$$E_a = \alpha \Delta E + \text{const.}, \quad (11)$$

where  $\alpha = -RT/K$  and  $\text{const} = RT - E_D$ . This relation has the form of the empirical Brønsted–Polanyi equation which expresses the linear relation between the activation energy of surface reaction  $E_a$  and surface energy  $\Delta E$ .

*The authors thank Prof. Q. D. Trieu from the Institute of Chemistry, National Centre for Scientific Research, Hanoi and Dr I. Samohýl from Prague Institute of Chemical Technology for their comments and discussions.*

#### REFERENCES

1. Jungers J. C. et al.: *Cinétique Chimique Appliquée*. Société des Éditions Technip, Paris 1958.
2. Boreskov G. K.: *Kataliz. Voprosy teorii i praktiki*. Nauka, Novosibirsk 1987.
3. Quang N. X., Samohýl I., Thoang H. S.: *Collect. Czech. Chem. Commun.* 53, 1620 (1988).

Translated by J. Linek.