

Letter

# On the application of transition state theory to heterogeneous catalytic reactions

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## Abstract

A recent extension of the transition-state theory [Rooney, *J. Mol. Catal. A* 96 (1995) L1] is shown to be incorrect and contradicting with the basic principles of the transition-state theory (TST). © 1997 Elsevier Science B.V.

*Keywords:* Transition-state theory

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## 1. Introduction

Exact knowledge of the rates of chemical reactions is of immense practical and theoretical importance and one of the main tasks of chemical kinetics as a science is to determine them. In fact this task can be separated into two parts. First is the estimation of the rates of elementary reactions (e.g. rate constants and activation energies) and second is the calculation of rates of complex reactions, based on the knowledge of the rates of the elementary ones. The second task is even more important for heterogeneous catalysis where the law of active surfaces, introduced by Langmuir, explicitly requires several steps (at least adsorption and surface reaction), which are not a necessity for homogeneous reactions.

The cornerstone of modern chemical kinetics, besides the mass action law and the law of active surfaces (for heterogeneous catalysis), is the Arrhenius equation for reaction rate constants. Estimation of activation energies requires the knowledge of the potential energy surface and is a formidable task to be solved by quantum chemistry.

The pre-exponential factor in the Arrhenius equation was treated successfully by Eyring [1] and Evans and Polanyi [2] in 1935 within the framework of the transition state theory (TST). This theory explained the mass action law, and rate constant dependence on temperature and provided possibilities for the estimation of pre-exponential factors in good agreement with experimental data. Later, Temkin [3] and Laidler et al. [4] applied the TST to processes on surfaces.

Initial application of the TST to heterogeneous catalysis required some additional assumptions [3]. For instance, random distribution

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of molecules was assumed, and the number of activated complexes was considered to be small in comparison with the total number of surface sites. Special assumptions were introduced with respect to the geometry of reactants and activated complexes on the surface. Many different contributions to the TST were made over the years and they are briefly described by Laidler [5].

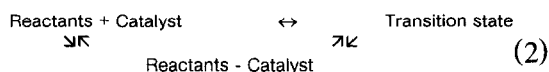
## 2. Treatment of Rooney [6]

Recently an 'extension' of the TST was proposed by Rooney [6]. It was suggested that equilibrium between free reactants and catalyst-reactant complexes together with the equilibrium between complexed reactants and the transition state should be taken into account. The idea of the author [6,7] is that the equilibrium constant  $K^\ddagger$  in the famous TST equation

$$k = kT/hK^\ddagger \quad (1)$$

is a composite constant, e.g. a multiple and/or quotient of all the individual equilibrium steps.

The following scheme was considered



It was stated that if there is a physical equilibrium between free reactants and complexed or chemisorbed reactants, then the free reactants plus catalyst are also in physical equilibrium with the transition state complex.

The author [6] believed that he introduced a novel combination of Langmuir and Eyring theories, thus giving a new explanation to the well-known compensation effect, i.e. the relation between experimentally observed Arrhenius parameters (pre-exponential factor and activation energies) for either the same reaction over similar catalysts or for the same catalyst and a group of similar reactions. Such a dependence was observed not only for catalytic, but also for thermochemical and photochemical reactions [8].

The aim of the present note is to discuss the assessments in Refs. [6,7].

## 3. Compensation effect and multistep reactions

It was realized many years ago [9,10] that compensation effects can be considered either based on analysis of multistep complex reactions or only treating elementary reactions. The supposition that if the compensation effect exists it cannot be attributed to an elementary process was in fact introduced at least 40 years ago [9]. More recently, it was pointed out more by Bond [11] that very frequently observed correlation in the literature between the activation energy and the pre-exponential factor arises from the use of apparent rather than true activation energies, with the most common explanation for that being either the surface heterogeneity or the occurrence of two or more concurrent reactions [12].

Although many attempts have been made to explain the compensation effect within the framework of the TST, the effect itself does not follow from the conventional TST, (e.g. any connection between activation entropy and activation enthalpy).

The idea that the compensation effect is due to the multistep nature of catalytic or, in general, chemical reactions, although not new, probably in many cases is quite acceptable. As an example of such an approach one can mention an excellent analysis [13] of kinetics of metal-catalyzed reactions of alkanes, where appearance of apparent compensation effect (definition from Ref. [13]), arising from a multistep reaction mechanism, was convincingly demonstrated.

What should be doubted, however, is the manner of deriving the kinetic equations, proposed in Refs. [6,7] and the attempt to link the TST with the theory of complex reactions on a level of an elementary reaction.

The kinetics of complex reactions is an advanced field of chemical kinetics [5,14]. The methods of deriving such equations and the application to catalytic kinetics have been discussed numerous times in textbooks. Let us consider a simple sequence of equilibrium adsorption (A) and reaction (R) steps



where S is the substrate, P the product, and Z the surface site. The adsorption coefficient  $K_S$  is expressed

$$K_S = \theta_S / (P_S \theta_O) \quad (4)$$

where  $P_S$  is the partial pressure of substrate S. The overall reaction rate can be expressed according to the law of active surfaces

$$r = k_R \theta_S \quad (5)$$

where according to the conventional TST

$$k = \chi kT / hK_{\ddagger} \exp(-E_a/RT) \quad (6)$$

where  $K_{\ddagger}$  is the equilibrium constant, which is the ratio of corrected partition functions of activated complexes and the adsorbed component S.  $\chi$  is the transmission coefficient which is due to the fact that the probability of activated complexes going into products is not equal to unity (e.g. activated complexes formed from reactants may not pass at once into products).

From Eqs. (4) and (6) and the balance equation

$$1 = \theta_S + \theta_O \quad (7)$$

we arrive at

$$r = \chi kT / hK_{\ddagger} \exp(-E_a/RT) K_S P_S / (1 + K_S P_S) \quad (8)$$

Eq. (8) is in fact the same equation as given in Ref. [7] and it strictly follows from conventional assumptions of the TST and LAS.

We conclude that an extension of the TST [6,7] deals with a combination of several elementary steps, which is a contradiction in terms, as the TST applies only to single elementary reactions. It is evident, that there was no need in introduction in Refs. [6,7] of extensions in the conventional TST for the purpose of explaining the compensation effect in case of complex, multistep reactions.

## References

- [1] H. Eyring, *J. Chem. Phys.* 3 (1935) 107.
- [2] M.G. Evans, M. Polanyi, *Trans. Faraday Soc.* 31 (1935) 875.
- [3] M. Temkin, *Zh. Fiz. Chim.* 11 (1938) 169.
- [4] K.J. Laidler, S. Glasstone, H. Eyring, *J. Chem. Phys.* 8 (1940) 659.
- [5] K.J. Laidler, *Chemical Kinetics*, Harper Collins, 1987.
- [6] J.J. Rooney, *J. Molec. Catal. A. Chem.* 96 (1995) L1.
- [7] W.R. Patterson, J.J. Rooney, *J. Catal.* 146 (1994) 310.
- [8] W. Linert, R.F. Jameson, *Chem. Soc. Rev.* 18 (1989) 477.
- [9] S.L. Kiperman, *Introduction Into the Kinetics of Heterogeneous Catalytic Reactions*, Moscow, Nauka, 1964.
- [10] S.L. Kiperman, *Foundations of Chemical Kinetics in Heterogeneous Catalysis*, Moscow, Chimia, 1979.
- [11] G.C. Bond, *Catal. Today* 17 (1993) 399.
- [12] A.K. Galwey, *Adv. Catal.* 26 (1977) 247.
- [13] G.C. Bond, A.D. Hooper, J.C. Slaat, A.O. Taylor, *J. Catal.* 163 (1996) 319.
- [14] M.I. Temkin, *Adv. Catal.* 28 (1979) 173.