

ON THE METHODOLOGICAL PRINCIPLES OF STUDYING THE MECHANISMS OF PHYSICO-CHEMICAL PROCESSES THROUGH RATE CONSTANTS

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Abstract. *The article briefly describes a method for studying their energy, thermodynamic and kinetic parameters, and explains almost all processes in terms of chemical reactions. When studying the mechanisms of physicochemical processes, determining their kinetic and thermodynamic parameters, it was argued that the method for determining the rate constants of chemical reactions is the most effective.*

Keywords: *monomolecular, bimolecular, polymolecular, energetic, kinetic, physical, chemical, mathematical, geometric, models, enthalpy, entropy.*

Introduction

Sciences of the 11th century and their research areas are developing with the deepening of the integration of natural and exact sciences and the application of IT technologies to them. A clear example of this is the creation and development of dozens of sciences such as physical chemistry, chemical physics, astrophysics, biophysics, and biochemistry.

Previously, we explained some of our opinions that it is possible to calculate energetic and kinetic parameters by explaining physical processes in terms of "monomolecular", "bimolecular", "poly-multimolecular" chemical reactions, depending on the number of molecules or particles involved in them, and to explain their physical mechanisms [1].

Indeed, the processes occurring in nature cannot be studied in detail without physical, chemical, mathematical, geometric and logical modeling [1-4].

Methods and Results

Any process, despite the complexity of the time and mechanisms of its occurrence, can be explained with the same success in terms of chemical reactions. For this, it is enough to visualize the processes using models of at least two energy states. In classical concepts, the energy states of this process are described as follows in the first approximation (Fig. 1).

Yedas - the energy of the "initial substance", the energy of the "subsequent products" formed as a result of a single reaction, YE_{\neq} - the total energy of the active complex, A - system or the initial state of the substance, B - the state of the system or substance after the reaction or process, K_{\neq} is the unbalanced state of the active complex, EA - the energy corresponding to the energy "barrier" value for the transition of the initial substance to the active complex, EA' - the total energy released or absorbed during the transition of the active complex to the next product, $\Delta U = \Delta E$ - initial and final state (product) energy difference.

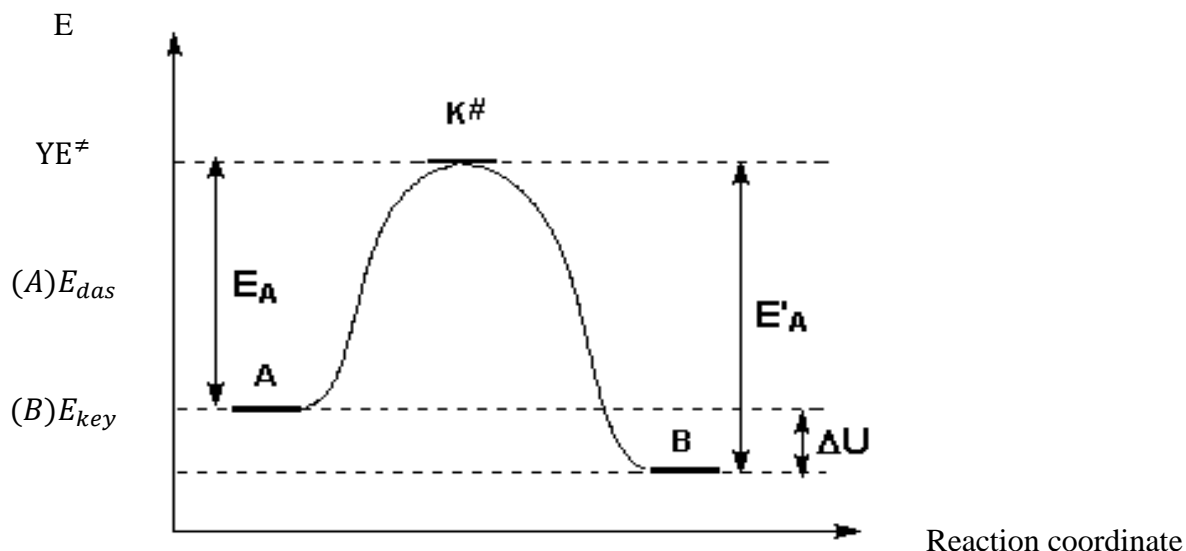


Figure 1. Dependence of process energy on coordinate

Let's imagine that a body or system goes from state A to state B and vice versa from state B to state A. This process can be formally described in terms of chemical reactions as follows:



Such monomolecular reactions occur with a certain energy effect ΔE . Here, ΔE is characterized by the difference in the energies of two energetic states. In quantum visualizations, this situation is easier to explain. The system moves from a lower energy state to a higher energy state as a result of absorbing or releasing energy ΔE and vice versa.

Monomolecular reactions:



is depicted in the (1) form.

And bimolecular reactions,



is described in appearance, etc.

Physical or biological processes are explained in terms of such mono- or multi-molecular chemical reactions, and energetic, thermodynamic and kinetic parameters are determined by applying the Arrhenius equation to them. Knowing ΔE , all thermodynamic parameters can be calculated using the following equations.

Enthalpy:

$$\Delta H = \Delta E - RT \quad R = 0.002 \text{ kcal/mol. grad} \quad (2)$$

Entropy:

$$\Delta S = R \left[\ln Z - \ln \frac{kT}{h} - 1 \right] \quad (3)$$

Gibbs potential:

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

It should be noted that in most articles the units of physical quantities are given in different systems, as a result of which confusion occurs in calculations.

Suppose a monomolecular process represented by formula (1) is taking place. In that case, the constants of forward and reverse reactions of such a process are determined by k_1 and k_2 , respectively. In turn, reaction constants can be expressed and determined by the following Arrhenius equation

$$k = Z_0 e^{-\Delta E/RT} \quad (5)$$

In this expression ΔE^\ddagger -activation (activation) energy is called. Z_0 is the frequency factor and is determined from the graph $k=k(1/T)$. For small temperature intervals ΔT , it is possible to calculate ΔE by determining k corresponding to temperatures T_1 and T_2 .

From this value of the activation energy, it is possible to determine the thermodynamic parameters of this process from the above expressions. But in the study of many physico-chemical processes, in practice, it is enough to study only the dependence of k on pressure, temperature, and concentration. To be more precise, it would be more correct to say that it has become a classic way to limit oneself to such an approach. Such limitation cannot provide sufficient information about the mechanisms and kinetics of the studied processes. Therefore, by the 80s of the last century, he was a professor at MSU.

A new theory of the rate constant of chemical reactions was proposed by M. I. Shakhparonov [2]. According to this theory, in order to obtain more detailed information about the mechanisms of physico-chemical processes, it was considered more appropriate to study their thermodynamic parameters in depth.

Based on the new theory, the formula for the dependence of the speed constant of chemical reactions called the transmission coefficient α on the quantity was derived, and the formulas for calculating all the quantities included in this formula, including the thermodynamic parameters enthalpy, entropy, Gibbs potential, and the empirical and theoretical values of the transmission coefficient α were consistently derived. As a result, it was proved that the transmission coefficient for many reactions is much smaller than one, $\alpha \ll 1$. This theory was recognized as a new method of studying the molecular structure of substances, the kinetics and mechanisms of processes occurring in them. The transmission coefficient α , in particular, expresses the probability of how much of the "active complex" formed in the chemical process turns into a new product.

The basic equation of the theory of absolute rates of reactions is generally expressed as follows:

$$k = \alpha_0 \frac{k_b T}{n} \text{yexr}(-\Delta G^\ddagger / RT) \quad (6)$$

where α is the transmission coefficient, k_b is the Boltzmann constant, ΔG^\ddagger is the Gibbs potential (reaction enthalpy), k is the rate constant of the process (reaction). The stage of the active complex formation reaction can be described as follows:



The activation enthalpy ΔG^\ddagger , the standard enthalpy ΔH^\ddagger , and the entropy ΔS^\ddagger are related by equation (4). From these, equation (6) can be written as follows:

$$k = \alpha_0 \frac{k_b T}{n} e^{\Delta S^\ddagger / R} \cdot e^{-\Delta H^\ddagger / RT} \quad (8)$$

This equation corresponds to the Arrhenius equation for a small temperature range, because in these cases the second exponent $e^{-\Delta H^\ddagger / RT}$ is equal to the first exponent $\alpha_0 \frac{k_b T}{n} e^{\Delta S^\ddagger / R}$ limit is almost independent of temperature.

In this case, from equation (8):

$$\Delta H^\ddagger = RT^2 \left(\frac{\partial \ln k}{\partial T} \right)_p - RT - RT^2 (\sum \Delta V_i) \left(\frac{\Delta \ln p}{\partial T} \right)_p \quad (9)$$

the equation is derived, where k is the following reaction rate constant in terms of chemical reactions

$$\sum_i \nu_i M_i \Leftrightarrow \sum_i \nu_i M_i \quad (10)$$

As can be seen from the equation (9), the enthalpy ΔH does not depend on the transmission coefficient. The third term r is the density of the substance and depends on the temperature. Such a connection makes it possible to determine the thermal coefficient of volume expansion of the substance from the experiment with great accuracy.

Discussions

If k is known from experience, ΔH can be calculated from equation (9). But to calculate ΔG^\ddagger or ΔS^\ddagger , there should be information about the transmission coefficient α . The classical theory of the absolute rate of reactions (RATKN) does not allow to calculate the true value of the transmission coefficient. In practice, RATKN is taken as $\alpha=1$ in calculations. In this case, the ΔG^\ddagger and ΔS^\ddagger found can be very different from the true values, because often $\alpha \ll 1$ for many reactions. This value was confirmed to be smaller than $\alpha \sim 10^{-2}-10^{-9}$ for many reactions (processes) studied in detail [2,3]. Imagine the difference between $\alpha=1$ and $\alpha \sim 10^{-2}-10^{-9}$.

Methods of experimental study of active complexes were not known until recently. And quantum mechanical calculations are very complicated. Derivation of the main equation of RATKN, ways of derivation of equation (8) are sufficiently covered in chemical kinetics textbooks. Based on the postulates of the theory of the absolute rate of reactions, it is assumed that the active complex A^\ddagger is in thermodynamic equilibrium in the reaction environment. In fact, the reaction involving the active complex takes place in the simplest form in two steps:



In that case, statistical methods are used to determine equations (6) for the rate constant k and the reverse reaction constant k' . Earlier calculations were performed only for an ideal gas. The new theory makes it possible to determine the true values of all thermodynamic and kinetic parameters for processes occurring in substances in almost any phase.

In the results of theoretical and experimental studies conducted using independent methods of the processes occurring in a large number of studied gases and liquids, it was observed that all physical parameters calculated within the error level are in perfect agreement [3-9].

Conclusions

By explaining almost all processes in terms of chemical reactions, the method of studying their energetic, thermodynamic and kinetic parameters was briefly described.

In studying the mechanisms of physico-chemical processes, determining their kinetic and thermodynamic parameters, it was proved that the method of determining the rate constants of chemical reactions is the most effective.

In the classical theory of the rate constant of chemical reactions, the value of the transmission coefficient α was considered to be practically always equal to one, but the new theory proved that it often has values much smaller than one.

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