E.N. YEREMIN

THE FOUNDATIONS OF CHEMICAL KINETICS

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Translated from the Russian
by
ARTAVAZ BEKNAZAROV

MIR PUBLISHERS · MOSCOW

First published 1979
Revised from the 1976 Russian edition

На английском языке

© Издательство «Высшая школа», 1976

© English translation, Mir Publishers, 1979

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ОСНОВЫ ХИМИЧЕСКОЙ КИНЕТИКИ

Издательство «Высшая школа»
Москва

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To the memory of my daughter,
Irina

Preface

This textbook has emerged from the lectures on chemical kinetics given by the author for more than 15 years for chemistry students at the Moscow State University as part of a general course in physical chemistry. Much space in the book is devoted to the fundamental concepts and therefore it may serve as an elementary textbook. On the other hand, the book provides a more detailed treatment of some theoretical problems than is found in ordinary courses of physical chemistry. Thus, the section dealing with unimolecular reactions has been considerably augmented; an example is a detailed account of the Slater theory.

Furthermore, the author has found it useful to supplement the treatment of the various aspects of the theory of the activated complex (transition-state theory) with concrete examples of the application of this theory to bimolecular reactions involving complexes of various configurations, the results of calculations being compared with the theory of activated collisions. This information must be helpful in applying the theory of kinetics in practical work. The exposition of the principles of transition-state theory is preceded by Chapter 5 which is devoted to the foundations of statistical thermodynamics. The experience of teaching physical chemistry at the Chemistry Department has shown that this chapter may be self-contained in a study of the fundamentals of thermodynamics.

Separate chapters are concerned with the kinetics of photochemical reactions and reactions taking place in electrical discharges. The inclusion of these topics may evidently be partly explained by the author's personal tastes and the trend of his work in the corresponding fields of chemical kinetics.

Reactions in solutions and homogeneous catalysis in solutions are treated in Chapter 12. Here much attention is paid to the theory of intermediates and, in particular, to the classical works of E. I. Shpitalsky, a Professor of Moscow University.

The author has deliberately avoided expounding heterogeneous catalysis, an area so wide that it would have increased the size of the book three times at least, among other things.

The book is intended both for a beginning student of chemical kinetics at chemistry and chemical-engineering higher schools and for a more thorough study of the subject. It may be found useful by post-graduates and also by all those who wish to study chemical kinetics.

In preparing this second edition I have taken into account all the comments made by my colleagues; also, all the misprints have been corrected and I have included a new section devoted to methods of measurement of reaction rates and of determination of reaction order and also chapters on the kinetics of topochemical processes.

In conclusion, the author extends his sincere thanks to E. A. Rubtsova and V. M. Belova who have been kind enough to offer their help in preparing this manuscript.

E. N. Yeremin

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CHAPTER 1

Basic Concepts and Empirical Relationships

Physical chemistry is concerned with study of chemical systems (i. e., systems in which chemical reactions take place) mainly from the standpoint of thermodynamics and kinetics. The *thermodynamic* treatment based on the study of the energetic properties of a system and its entropy allows one to determine the *possible* final result of a chemical interaction. Very often the conclusion made as to the possibility of a reaction does not mean that the chemical reaction of interest to us will really be accomplished under given conditions. For example, a thermodynamic study of the system

$$\text{C (graphite)} \longrightarrow \text{C (diamond)}$$

that is, the transformation of one crystalline modification of carbon (graphite) into another modification, diamond, shows that under ordinary conditions (298.15 K and 1 atm) graphite is more stable than diamond, i.e., that there exists the following inequality of the chemical potentials:

$$\mu_{\text{graph}} < \mu_{\text{diam}} \tag{1.1}$$

and there must occur a spontaneous transformation of diamond into graphite. We know, however, that this is not the case in actuality. Such a contradiction between theoretical inferences and practical observations is associated with the limitedness of the thermodynamic method which is concerned only with the initial (graphite) and final (diamond) states of the system. Indeed, under ordinary conditions the molar free energy of graphite is lower than the free energy of diamond. These energy relations may be explained graphically (Fig. 1.1).

The point, however, is that the real process of recrystallization, i.e., the conversion of a crystal lattice of the diamond type into that of the graphite type involves of necessity certain intermediate steps. The formation of intermediate structures, which originally constituted the distorted lattice of diamond, is associated with the consumption of energy amounting to $G^{\neq}$. Therefore, the actual change of the energy during the course of the process will be depicted by a curve with a maximum. The height of the maximum as compared with the energy of the original configuration (diamond), $\Delta G^{\neq}$, may be called the **free energy of activation.**

In other words, the thermodynamically possible transition of the system from the initial to the final state requires that a certain energy barrier be overcome, a barrier that hinders the real occurrence of the process, especially at low temperatures. At higher temperatures, the atoms in the crystal lattice move more rapidly and have more energy, and therefore the attainment of the intermediate configuration—the passage over the energy barrier—is facilitated. Indeed, at sufficiently higher temperatures diamond turns spontaneously into graphite.

From the foregoing it must be clear that thermodynamics, which does not deal with intermediate states and is concerned only with comparing the initial and final states, can provide no information about the actual feasibility of a thermodynamically possible process.

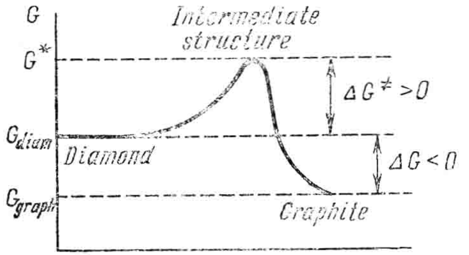

Fig. 1.1. Changes in the Gibbs free energy during the transformation of diamond to graphite at 298.15 K and 1 atm (an arbitrary scale).

Returning to the thermodynamic method of investigation, it is possible to find conditions for the equilibrium coexistence of graphite and diamond; they are known to be characterized by the equality of the chemical potentials:

$$\mu_{\text{graph}} = \mu_{\text{diam}} \tag{1.2}$$

At a temperature of 298.15 K (according to an approximate calculation), it will suffice to compress graphite up to 15,000 atm. Beginning from this point, the spontaneous transformation of graphite into diamond becomes possible. But even at higher pressures when

$$\mu_{\text{graph}} > \mu_{\text{diam}} \tag{1.3}$$

the process does not take place at all or proceeds at such a slow rate that it is practically impossible to detect the appearance of the diamond structure. The cause of this lies in the same difficulty of surmounting the energy barrier at low temperatures. Recrystallization proceeds easily at high temperatures, of the order of 2000 K, but under these conditions the inequality (1.3) necessary for the formation of diamond requires a considerably higher pressure (more than 45,000 atm).

Thus, thermodynamics makes it possible to judge, on the basis of the energetic properties of a system and its entropy, about the *possible final outcome* of a chemical interaction, about the state of equilibrium. But it furnishes no information *on the time period* required for this result to be attained.

The time factor, a very important quantity in practice, is left out of an ordinary thermodynamic treatment. On the other hand, the occurrence of processes in time is the concern of the thermodynamics of non-equilibrium processes (see Chapter 14).

Many examples could be cited, in which thermodynamically possible processes do not practically occur because of negligibly low rates. Thus, the reaction between hydrogen and oxygen

$$2H_2 + O_2 \longrightarrow 2H_2O$$

is accompanied by a great loss of free energy:

$$\Delta G^0_{298} = -109.0 \text{ kcal}$$

At room temperature the equilibrium shifts almost completely to the side of formation of water. It is known, however, that the oxyhydrogen gas may stand for an indefinite period of time without the noticeable formation of water. The point here again is a high energy barrier, the necessity to consume a high amount of energy for the intermediate states to be formed. But as soon as a *catalyst* (sponge platinum) is introduced into the oxyhydrogen gas, the reaction will occur with a very high velocity, with an explosion.

It is therefore clear that the study of chemical systems from a thermodynamic standpoint alone is insufficient. No less important is their study from the viewpoint of the rates of processes, from the standpoint of *kinetics*, which is thus of great practical importance since it determines the feasibility of various chemical reactions, the fundamental possibility of which has been established thermodynamically.

Secondly, kinetics is of great theoretical importance since it allows one to get a deeper insight into the mechanism of reactions, i.e., to determine, more or less reliably, the intermediate reaction steps on the way to the end product. Thus, the study of kinetics of the formation of water shows that in the first stages there appear *free atoms and radicals* which are chemically highly active and readily enter into further conversions:

(1) the appearance of a free hydroxyl group:

$$H_2 + O_2 \longrightarrow 2OH$$

(2) the dissociation of the hydrogen molecules upon collision with a particle:

$$H_2 + M \longrightarrow H + H + M$$

(3) the formation of ozone and an oxygen atom:

$$O_2 + O_2 \longrightarrow O_3 + O$$

All these processes require a large quantity of energy (for example, for the dissociation of H_2 to take place, 103.5 kcal/mole of H_2 is required); the occurrence of these processes generates the reaction. This energy is consumed on surmounting the main energy barrier.

The activated particles formed in stages (1), (2) and (3) interact with bond-saturated molecules. These are the processes that continue and accelerate the reaction:

$$(1)\ OH + H_2 \longrightarrow H_2O + H$$

$$(2)\ H + O_2 \longrightarrow OH + O$$

$$(3)\ O + H_2 \longrightarrow OH + H$$

Finally, an important part is played by processes in which the active particles perish, as a result of which the reaction may be brought to completion without an explosion.

A distinction is made between the processes in which atoms and radicals are destroyed *at the walls* of the reaction vessel:

$$(4)\ H + H + \text{wall} \longrightarrow H_2 + \text{wall}$$

$$(5)\ OH + H + \text{wall} \longrightarrow H_2O + \text{wall}$$

and those in which they are destroyed *in the bulk*:

$$(6)\ H + O_2 + M \longrightarrow HO_2 + M$$

The last equation should be considered in more detail. It describes the reaction during the course of a triple collision, i.e., a collision of three particles (also called a ternary or three-body collision): a hydrogen atom, an oxygen molecule and a third particle (a molecule), the participation of which is necessary for the stabilization of the newly formed molecule—the radical HO_2, by way of removal of the energy.

It is interesting that the formation of the free radical HO_2 was originally postulated with the purpose of explaining some of the observed specific features of the oxidation of hydrogen. The activity of the particle HO_2 was assumed to be low since only in isolated cases does it continue the reaction; its formation mainly implies the removal of a considerably more active particle—the hydrogen atom. The formation and existence of the free radical HO_2 was later confirmed by direct experimental observations. Thus, the discovery of the radical HO_2 was made as if at the tip of the pen.

1.1. Basic Concepts and Definitions

Let us first define the rate of a reaction. The rate of a reaction in gas mixtures and in liquid solutions is defined as **the rate of change of the amount of one of the reactants or products per unit volume per unit time.** The change of the quantity of a given substance in the system per unit time may be expressed by the derivative dN/dt, where N is the number of moles of the substance and t is the time. If we denote the volume of the system by V, then the instantaneous (true) rate * will be defined by the following relation:

$$w = \pm \frac{1}{V} \cdot \frac{dN}{dt} \tag{1.4}$$

In this expression the plus sign applies to products since their concentration increases with time; the minus sign is used for reactants because their concentration decreases with increasing time. Thus, the rate of reaction is always positive. Expression (1.4) is a strict definition of the reaction rate, which is applicable in a general case and for a system of variable volume. A simpler equation, however, is often used, which is suitable for a reaction in a system of constant volume. Since the ratio $N/V = c$, i.e., is equal to the concentration of the substance (its molarity), then at constant volume

$$w = \pm \left(\frac{dc}{dt}\right)_V \tag{1.5}$$

In this, simpler definition the reaction rate (at constant volume) is the *change* of the concentration of a given reactant or product in unit time. Equation (1.5) is evidently applicable to reactions in solutions without substantial reservations; it also applies to reactions involving gases provided that they take place in closed reaction vessels. With the volume being kept constant, expression (1.5) can be even more simplified:

$$w = \pm \frac{dc}{dt} \tag{1.6}$$

It is necessary to note that if the reaction taking place in a system involves several substances, for example, A, B, D, ..., E, F, that is,

$$\underset{c_1}{\nu_1\mathrm{A}} + \underset{c_2}{\nu_2\mathrm{B}} + \underset{c_3}{\nu_3\mathrm{D}} + \ldots \longrightarrow \underset{c_1'}{\nu_1'\mathrm{E}} + \underset{c_2'}{\nu_2'\mathrm{F}} + \ldots$$

(where c_is are the reactant concentrations at various elapsed times), then for the reaction rate to be determined unambiguously it will suffice to trace out the change in concentration of one of the reactants. The changes in the concentrations of the other reactants can always be found from the ratios of the stoichiometric coefficients v_i.

---

* In contrast to the so-called average rate.

Thus, for example, the rate for the reactant A

$$w = -\frac{dc_1}{dt}$$

is related to the rates with respect to the other reactants by the equation:

$$w = -\frac{dc_1}{dt} = -\frac{\nu_1}{\nu_2}\cdot\frac{dc_2}{dt} = -\frac{\nu_1}{\nu_3}\cdot\frac{dc_3}{dt} = \ldots = \frac{\nu_1}{\nu_1'}\cdot\frac{dc_1'}{dt} = \ldots \qquad (1.7)$$

1.2. The Basic Law of Kinetics. Effect of Concentration on Reaction Rate

If the temperature of the system is maintained constant, then the rate of reaction is determined by the concentrations of the substances making up the system. In the first place, one should speak of the concentrations of the reactants in a given reaction. However, the concentrations of the reaction products often has a bearing on the rate as well: if they accelerate the reaction, the term **autocatalysis** is used, and if the products slow down the reaction, the use of the term **autoinhibition** is justified. If the reaction rate is influenced by a substance (or a body) which is present in the system in an unchanged amount and which is not a direct participant in the reaction, then such a substance or body is called a **catalyst.**

A mathematical formula that relates the reaction rate to the concentrations is termed the **rate equation** or the **kinetic equation.** It is very important to note that in a general case the form of the kinetic equation cannot be predicted on the basis of the stoichiometric equation of the reaction. Thus, the reactions of hydrogen with iodine and bromine vapours are expressed by means of the same stoichiometric equations, but the kinetic equations used for them are quite different:

$$\text{for } H_2 + I_2 = 2HI \qquad \frac{dc_{HI}}{dt} = kc_{H_2}c_{I_2}$$

$$\text{for } H_2 + Br_2 = 2HBr \qquad \frac{dc_{HBr}}{dt} = \frac{kc_{H_2}c_{Br_2}^{1/2}}{1 + k'\dfrac{c_{HBr}}{c_{Br_2}}}$$

The difference in the rate equations is accounted for by the difference in the reaction mechanisms.

The basic law of kinetics (the **Law of Mass Action**) follows from a large body of experimental data and expresses the dependence of the reaction rate on concentration:

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