

# THEORY OF PHYSICAL CHEMISTRY PROCESSES AT A GAS-SOLID INTERFACE

TOVBIN

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ADVANCES IN  
SCIENCES AND TECHNOLOGY  
IN THE USSR

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YU. K. TOVBIN

Translated from the Russian by G. Leib

Mir Publishers

Moscow

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CRC Press

Boca Raton Ann Arbor Boston London

**Advances  
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Science  
and  
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**Chemistry Series**



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## Preface

The surface processes at a gas-solid interface can be either an independent object of investigation or a constituent part in the investigations of many practical applications. They include the adsorption of gas-phase molecules, migration of adsorbed particles, reactions between adsorbed particles and between adsorbed particles and atoms of the solid, the dissolution of adsorbed particles, surface segregation of components of the solid, processes causing motion of the phase interface, and so on. The enumerated processes have a general nature and are realized on the surfaces of all solids such as metals, alloys, and variable composition compounds. The occurrence of a surface process may change the state not only of the surface and subsurface region, but also of the entire bulk of the solid.

The task of the theory of physicochemical processes is to give a quantitative description of the state of a system for known external conditions and a characteristic time scale. A gas-solid system is a condensed one, hence when constructing a theory of physicochemical processes the methods of the theory of a condensed state must be used. Condensed systems are featured by the determining role of the interactions between particles. The calculations of these interactions are based on the quantum theory, but its practical application encounters many difficulties. In practice, more approximate models of particle interactions are employed, namely, model or empirical potentials whose parameters are determined by fitting the predicted characteristics of a system to the experimental ones.

All the above processes occurring at a gas-solid interface can be described from a single standpoint corresponding to the atomic-molecular level of the statistical theory (or simply to the molecular level, although atoms, ions, radicals, or molecules can be the particles in question) using model interaction potentials. The present book is devoted to such a single approach for constructing mathematical models of the physicochemical processes in a gas-solid system with a view to its chief real properties—the interaction between all the components and the inhomogeneity of the system. Two problems had to be solved to take these real factors into account: it was necessary to construct a theory of chemical kinetics considering the interaction between all the components of a reaction system and a theory describing the distribution of the interacting particles by the sites of inhomogeneous lattices. These problems were solved by employing the cluster approach. It is set out from simple cases to more involved ones so that the reader will be able to master the method

and use it independently for constructing equations describing processes occurring on the surface and in the subsurface region of a solid. The usual knowledge acquired at higher schools is sufficient for mastering the cluster approach. The intermediate transformations are given in detail to curtail technical difficulties.

The book is intended for a broad circle of specialists in physical chemistry dealing with surface phenomena, adsorption, heterogeneous catalysis, gas chromatography, and the growth of crystals from the gas phase. It is also intended for post-graduates and senior students specializing in physical chemistry and related subjects. Experimenters will obtain notions on the physical fundamentals of molecular-kinetic models of surface processes, on the field of application of the traditionally employed models, and on the possibilities placed at their disposal by modern statistical physics, while specialists in mathematical modelling can use the material for constructing mathematical models for a broad range of processes being studied.

The first chapter introduces the basic notions of a gas-solid interface, the fundamental concepts of lattice systems and multiparticle distribution functions that are used later on. Chapters 2-7 can be divided conditionally into two parts. In Chapters 2-5, the cluster approach is employed for the simplest interaction potential—the interaction of the nearest neighbors. This simplifies acquaintance with the new method and enables one to reveal the general laws of models of nonideal systems. These laws are usually hidden by the specific nature of the particle interactions in the bulk of a solid, on its surface, and between the adsorbed particles. In Chapters 6 and 7, the cluster approach is used for more complicated potentials—the two-body potential with an arbitrary finite radius of interaction and multiparticle potentials.

The paramount task of the molecular-kinetic theory of processes in condensed phases consists in describing the distribution of particles, a knowledge of which allows one to calculate any thermodynamic characteristics of a system and the flows of particles. First the equilibrium distributions of particles on homogeneous (Chap. 2) and inhomogeneous (Chap. 3) lattices are considered, and then the kinetics of surface processes with fast (Chap. 4) and slow (Chap. 5) mobility of the particles. The distribution of particles with more involved interaction potentials is set out in the same sequence. The discussed models cover the entire time interval from the instant of contact of the gas phase with the solid, when the state of the latter does not have time to change under the influence of the gas molecules (a nonreorganizing surface), to the instant when this process terminates (a reorganized surface or bulk of a solid, or both).



The book deals with the adsorption of molecules of the gas phase, the diffusion of adsorbed particles over the surface and their dissolution in the bulk of the solid, catalytic processes, the motion of the phase interface when a crystal grows from the gas phase, the surface segregation of the components of alloys in vacuum and when they contact the gas phase. A detailed treatment of each of these topics, as well as topics such as the statistical theories of the condensed state, the theories of elementary processes in a condensed phase, and their applications is impossible within the small volume of the present book.



# Contents

1.	<b>Introduction</b>	11
1.1.	Gas-Solid Interface	11
1.2.	Tasks of the Theory of Physicochemical Processes	17
1.3.	Local Configurations of Particles	21
1.4.	The Cluster Approach	29
1.5.	Ideal Models	32
2.	<b>The Equilibrium State of Homogeneous Systems</b>	45
2.1.	Homogeneous Systems	45
2.2.	Distribution of the Particles in a Binary Solution	48
2.3.	Isotherm and Heat of Adsorption	55
2.4.	Particle Distribution in a Multicomponent Solution	65
2.5.	Adsorption and Absorption of a Gas Mixture	69
3.	<b>The Equilibrium State of Inhomogeneous Systems</b>	75
3.1.	Inhomogeneous Systems	75
3.2.	Distribution of Particles of a Two-Component Solution	84
3.3.	Adsorption Isotherms	90
3.4.	Heat of Adsorption	96
3.5.	Ordering of Adsorbed Particles	103
3.6.	Distribution of Multicomponent Solution Particles and Adsorption Isotherms of a Gas Mixture	107
3.7.	Absorption of Gas-Phase Molecules	112
3.8.	Solid-Vacuum Interface	116
3.9.	Solid-Gas Phase Interface	121
4.	<b>Rates of Surface Reactions. Fast Mobility of Reactants</b>	125
4.1.	The Fundamental Kinetic Equation	125
4.2.	One-Site Reactions	127
4.3.	Two-Site Reactions	137
4.4.	Kinetic Equations of Nonideal Reaction Systems	143
4.5.	Inhomogeneous Systems	147
4.6.	Reactions in Inhomogeneous Systems	155
5.	<b>Surface Processes. Slow Mobility of Particles</b>	159
5.1.	Kinetic Equations of Processes	159
5.2.	Local Redistribution of Particles	163

5.3.	Models of Surface Processes	168
5.4.	Evolution of the Concentration Profile in the Subsurface Region of a Solid	175
5.5.	Rough Gas-Solid Interface	180
5.6.	Dissolution of Adsorbed Particles	186
5.7.	Diffusivities	189
6.	<b>Equilibrium of a Gas-Solid System</b>	193
6.1.	Two-Body Interactions of a Finite Number of Neighbors	193
6.2.	Equilibrium Characteristics of Sorption	198
6.3.	Equilibrium State of Inhomogeneous Systems	205
6.4.	The Ordering of Particles in Sorption Problems	210
6.5.	Influence of a Gas on the State of a Solid	213
6.6.	Multiparticle Interactions	218
7.	<b>Evolution of a Gas-Solid System</b>	225
7.1.	Kinetic Equations. Two-Body Interaction Potential	225
7.2.	Surface Reactions	238
7.3.	Processes with Slow Particle Mobility	253
7.4.	Multiparticle Interactions in the Kinetics of Adsorption	260
8.	<b>Conclusion</b>	265
Appendix 1.	<b>Approximate Systems of Equations</b>	277
Appendix 2.	<b>Particle Interactions in the Kinetics of Surface Processes a Review)</b>	287
Appendix 3.	<b>Hierarchy of Mathematical Models of Surface Reactions</b>	309
Appendix 4.	<b>Designations of Particle Configurations and Their Probabilities</b>	321
	<b>References</b>	325
	<b>Index</b>	343

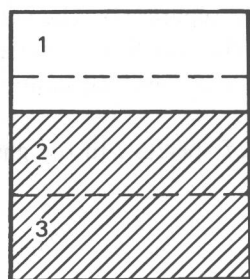
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## Introduction

### 1.1. Gas-Solid Interface

Let us consider a volume of space containing a part of the bulk phase of a solid, its surface, and part of the volume of a gas phase. This volume can be divided into three regions (Fig. 1.1). The singled out region of the solid has the same composition and distribution of its components as the remaining part of the solid. Similarly, the singled out region of the gas phase contains components in the same state as in the remaining part of this phase. The second region is one in which the composition and distribution of the particles differs from the other two phases. The molecular interpretation of a phase interface differs from the singling out of the dividing surface between two phases adopted in thermodynamics [1, 2]. It has a finite width which in the general case can change in time.

Let us discuss the main concepts and initial propositions used in the following.



**Fig. 1.1.** Gas-solid interface—region 2 (between the dashed lines);  
1—region of gas phase; 3—region of solid

**Gas Phase.** We shall limit ourselves to very simple notions of a gas phase as an ideal mixture of molecules [3, 4]. The total pressure  $P$  in a gas phase is determined as  $P = \sum_i P_i$ , where  $P_i$  is the partial pressure of the  $i$ -th component of the gas mixture;  $1 \leq i \leq s$ ,  $s$  is the number of components in the mixture. The partial pressure of a component is related to its concentration  $c_i$  by the expression

$$P_i = \beta^{-1} c_i \quad (1.1)$$

where

$$\beta = (N_A k_B T)^{-1} = (RT)^{-1} \quad (1.1a)$$

$$c_i = \frac{N_i}{V} \quad (1.1b)$$

Here  $k_B$  is the Boltzmann constant,  $N_A$  is the Avogadro constant,  $R$  is the molar gas constant,  $T$  is the absolute temperature,  $N_i$  is the number of molecules of species  $i$ , and  $V$  is the volume of the system.

The molecules of a gas phase are considered to be particles that do not interact with one another, and each of them is a statistically independent system. The statistical sum of a molecule of species  $i$  is

$$F_i^0(T) = \sum_n g_{in} \exp(-\beta E_{in}) \quad (1.2)$$

where  $E_{in}$  is the energy of a molecule of species  $i$  in the state  $n$ , and  $g_{in}$  is the degree of degeneracy of the given state. The energy of a molecule is usually represented as the sum of the relevant contributions of translational, rotational, and vibrational motions (if they can be separated). The calculation of the rotational and vibrational multipliers of the function of states of gas phase molecules is a quantum-statistical problem [5], and we shall assume them to be known.

The chemical potential of a molecule of species  $i$  in the gas phase can be written as follows:

$$\mu_{ig} = \mu_i^0 + \beta^{-1} \ln \frac{\beta P_i}{F_i^0} \quad (1.3)$$

where  $\mu_i^0$  determines the reference point. For a free particle in a gas phase,  $\mu_i^0 = 0$ , while if the adsorbed state is the reference one, we have  $\mu_i^0 = \varepsilon_i$ , where  $\varepsilon_i$  is the binding energy.

The influence of the nonideal nature of the gas phase is not considered in this book, but we shall note that the lattice model of the condensed state which is used can also be employed for these purpose [6-8].

**Solid.** We shall consider that the bulk of a solid is a homogeneous substitutional, interstitial, or mixed-type solution [9, 10]. We shall treat only the simplest Bravais lattices [11] in which depending on the temperature and concentration of the components their ordered arrangement is possible [12-14].

The nature of the distribution of the atoms in a solid solution depends on the interaction of its components. It is the simplest to consider the spectrum of possible distributions of the atoms for a binary alloy. We shall use the concepts of short-range and long-range order for their description. Short-range order characterizes the trend of local distribution of neighboring atoms of an alloy. The atoms of an alloy are said to tend to become ordered if the neighboring location of atoms of different species is more preferable than their chaotic arrangement, and they are said to tend to stratify if the neighboring location of atoms of one species is preferable.

In an equilibrium state, lowering of the temperature in the first case is attended by an ordered arrangement of the alloy atoms, and regular sublattices mainly filled with atoms of one species can be separated from the crystal lattice. The degree of deviation from this arrangement of the atoms characterizes long-range order. In the second case, lowering of the temperature is attended by the separation of a new phase, and the initially homogeneous phase becomes macroinhomogeneous.

In more complicated cases, different combinations of phase transitions of stratification and ordering are possible. For example, a system may pass over to a disordered and ordered phases or to two different ordered phases. The type of the phase transitions and the regions of their realization are determined by the concentrations of the components, the temperature, and the potentials of particle interaction. Similar transitions also occur in multicomponent solutions. An increase in the number of components increases the number of different combinations of the phase transitions [15].

**Subsurface Region of a Solid.** The nature of particle distribution near a surface generally differs from that in the bulk [16-20]. This difference is associated with the absence of a solid phase in the other half-plane. This disturbs the periodicity of the crystalline structure along a normal to the surface and results in a difference in the forces acting on an atom from the side of the other atoms of the alloy surrounding it on the surface and in the bulk (an atom in the bulk has more neighbors than one on the surface). As a result, a different distribution of the atoms ensuring a minimum of the free energy sets in in equilibrium.

The perturbation produced by a surface affects a subsurface region of a solid. Its width depends on the temperature, concentrations of the solid solution components, and on the potentials of particle interaction.

A very important characteristic of the subsurface region is the surface concentration of the atoms. For alloys, it is customary to speak of the surface segregation of the component whose surface concentration exceeds the bulk one. With an increase in the distance from the surface, the local concentrations of the particles tend to their bulk values. This also relates to the other characteristics of particle distribution determining short- and long-range orders, which in the subsurface region can have a great anisotropy.

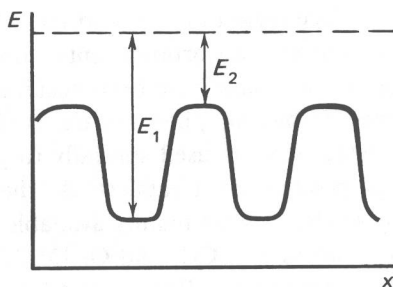
How the atoms of a solid are distributed in the subsurface region has a determining influence on all the surface processes: the surface composition determines the properties of the surface on which the gas-phase molecules are adsorbed and the surface reactions proceed, while how the atoms are distributed in the subsurface region governs the dissolution of the adsorbed particles and the rearrangement of the region itself.

A much more complicated situation is encountered for a "frozen" highly nonequilibrium state of a surface. Under these conditions, the ways of forming the surface are exceedingly important, namely, by splitting off part of a crystal in vacuum, sputtering onto a support, precipitation from a solution, sintering of a polycrystalline powder, etc. [21, 22], because the procedure employed to prepare a surface and the treatment of a specimen prior to running an experiment affect the state of the surface and the subsurface region first of all.

**Adsorption.** The surface atoms of a solid have a definite ability of forming bonds with molecules of the gas phase, which increases the concentration of these molecules near the surface [23-29]. The nature of the adsorption bond depends on the nature of the solid and the gas-phase molecules. It is customary practice to distinguish physical and chemical adsorption. In the former case, no collectivization of the electrons of the adsorbent and adsorbate occurs, while in the latter case a conventional chemical bond forms with redistribution of the electrons.

At the atomic level, the surface of a monatomic crystal is not homogeneous. It is a distributed system of atoms. The different positions of an adsorbed molecule over the adsorbent atoms are not equivalent energetically. The change in the binding energy when a molecule travels along a surface is shown schematically in Fig. 1.2. In a number of positions, its energy is minimal. Such positions and their environment form regions of localization of adsorbed molecules called adsorption centers of the surface. If the difference  $E_1 - E_2$  is large and is much larger than the thermal energy of the adsorbed particles,





**Fig. 1.2.** Potential relief of a homogeneous surface.

The dashed line depicts the energy of a free particle in a gas;

$E$  = activation energy of desorption;

$E_1 - E_2$  = activation energy of surface migration

the latter are predominately in the localization regions, and we have to do with localized adsorption. It generally occurs in chemical adsorption.

If the values of the energies  $E_1$  and  $E_2$  are close and have the order of magnitude of the thermal energy of the adsorbed particles, we have to do with non-localized adsorption. It occurs most frequently in physical adsorption. Here too lowering of the temperature may be attended by a transition from non-localized to localized adsorption (with disregarding of the tunneling effects possible for light particles [30, 31]). The nature of adsorption also depends on the state of the adsorbed particle. With a slow exchange of energy between a particle and the atoms of a solid, the particle may be in excited states [26, 32], which increases the degree of its delocalization.

Most solids have regions of localization of adsorbed particles with different binding energies on their surface. This is due to the different local chemical composition of the surface and a different geometric arrangement of the solid's atoms. Both these factors usually manifest themselves simultaneously. Such surfaces are said to be inhomogeneous. The scale of the inhomogeneities varies within broad limits from point imperfections and impurities to various macroregions [33, 34].

**Effect of Adsorbed Particles on the State of a Surface.** If the binding energy of an adsorbed particle to a surface is commensurable with the binding energy between the atoms of the solid, adsorption of molecules may cause substantial changes in the state of the surface. This is largely associated with the adsorbed particles compensating the absence of neighbors at the surface atoms. As a