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The Transition State in Surface Reactions

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The subject of the paper is the application of the method of the transition state (activated complex) to the calculation of the kinetics of chemical reactions on surfaces.

The schematic picture of the surface according to Langmuir is accepted as a basis, i. e. the surface is considered as an aggregate of identical elementary spaces retaining the adsorbed molecules, the forces of interaction between the adsorbed molecules being ignored.

A general statistical derivation of the Langmuir equation for adsorption equilibrium is given, including the adsorption of mixtures of gases, adsorption accompanied by dissociation and the statistical expression for the coefficient of adsorption (eq. 19). The type of adsorption where the molecule occupies two elementary spaces (eqs. 28 and 30) is considered.

The statistical method of considering adsorption equilibrium is applied to the calculation of the number of activated complexes on the surface, which determines the rate of the reaction. The formula obtained (eq. 35) gives a generalized „law of surface action“ of Langmuir and establishes the absolute magnitude of the rate constant. The agreement of the formula with experiment is illustrated by the example of the decomposition of PH_3 on glass.

Equations are given for the absolute velocity of activated adsorption on a bare surface. The dependence of the adsorption rate upon the extent of surface covering and the complications in the kinetics, arising when the mobility of the molecules or atoms on the surface is low, are considered.

1. Introduction

The method of the transition state or activated complex, developed by Eyring[1] and simultaneously by Evans and Polanyi[2],

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[1] Eyring, J. Chem. Phys., **3**, 107 (1935).

[2] M. G. Evans and Polanyi, Trans. Farad. Soc., **31**, 875 (1935).

determines the value of the pre-exponential factor in the Arrhenius equation for homogeneous reactions. It refines the results of the earlier theories, according to which this factor should be equal to the number of collisions for bimolecular reactions (Lewis[3], Hinshelwood[4]) and the vibration frequencies of the atoms of the molecule for unimolecular reactions (Herzfeld[5], Polanyi and Wigner[6]).

The fundamental equation of Eyring

$$k = \varkappa \frac{F_t'}{F} \frac{kT}{h} e^{-\frac{\varepsilon_0}{kT}} \tag{1}$$

expresses the rate constant k as a function of the height of the energy barrier ε_0, the product of the partition functions of the initial molecules F, the partition function of the transition state F_t' computed over all degrees of freedom except the „reaction path", and the transmission coefficient $\varkappa$ which may be taken equal to unity in the majority of cases. kT is the product of Bolzmann's constant and the absolute temperature; h is Planck's constant.

Equation (1) in a number of cases leads to results substantially at variance with the results of the primitive theories referred to above. For example, the rate of bimolecular association reactions in the case of complex molecules may be considerably less (10^6 times) than is to be expected according to the simple collision theory[7].

The subject of this paper is the extension of the transition state method to the kinetics of surface reactions. These include processes of activated adsorption, the reactions of gases with solids and chemical reactions on surfaces (heterogeneous catalytic processes).

The analogue of the simple collision theory for activated adsorption is the hypothesis that the rate of adsorption must be equal to the number of molecular impacts with the surface in unit

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[3] W. C. Mc. C. Lewis, J. Chem. Soc., **113**, 431 (1918).

[4] Hinshelwood, The kinetics of Chemical Change in Gaseous Systems, 3-d ed., Oxford (1933).

[5] Herzfeld, Ann. Phys., **59**, 635 (1919).

[6] Polanyi a. Wigner, Z. physik. Chem., A. „Haber-Band", 439 (1928).

[7] Bawn, Trans. Farad. Soc., **31**, 1536 (1935).

time, multiplied by $e^{-\frac{\varepsilon}{kT}}$, where ε is the energy of activation for adsorption. This hypothesis, however, has not been substantiated; the velocity of adsorption turns out to be less than this (Taylor[8], Leypunsky[9]) similarly to the case of bimolecular reactions referred to above.

The general formulation of the kinetics of reactions on surfaces has been given by Langmuir[10] in the form of „the law of surface action“ in analogy to the law of mass action. This formulation is based upon assumptions corresponding to the picture of „simple adsorption“, that is it is assumed that the surface contains a definite number of identical elementary spaces each of which can hold one molecule or atom, that the forces of interaction between adsorbed molecules can be neglected and only the interaction of the molecules with the surface is to be taken into account. With this assumptions the rate of the surface reaction

$$n_1A_1 + n_2A_2 + \ldots = n'_1A'_1 + n'_2A'_2 + \ldots$$

will be expressed in the following manner:

$$\omega = k\theta_1^{n_1}\theta_2^{n_2}\ldots\ldots \qquad (\text{if } \Delta n \leqslant 0) \qquad (2)$$

or

$$\omega = k\theta_1^{n_1}\theta_2^{n_2}\ldots\; \theta_0^{\Delta n} \qquad (\text{if } \Delta n > 0), \qquad (2a)$$

where $\theta_1, \theta_2 \ldots$ are the fractions of the surface occupied by the molecules of the substances $A_1, A_2 \ldots$; θ_0 is the fraction of the surface that is bare and Δn is the change in the number of molecules in the reaction

$$\Delta n = n'_1 + n'_2 + \ldots - n_1 - n_2 \ldots$$

It is not difficult to show that eqs. (2) and (2a) are in agreement with thermodynamics in the sense that they lead to the correct expression for the equilibrium conditions upon setting the rates of the direct and reverse reactions equal to each other.

Let us consider the reversible reaction

$$n_1A_1 + n_2A_2 + \ldots \rightleftarrows n'_1A'_1 + n'_2A'_2 + \ldots$$

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[8] Taylor, Trans. Farad. Soc., **28**, 131 (1932).

[9] Leypunsky, Acta Physicochimica URSS, **2**, 737 (1935); C. R. Acad. Sci. de l'URSS, **1**, 31 (1935); J. Phys. Chem. (Russ.), **9**, 143 (1937).

[10] I. Langmuir, J. Am. Chem. Soc., **38**, 2221 (1916).

Let $\Delta n = \Sigma n' - \Sigma n > 0$ for the given direction of the reaction. Then the condition for equilibrium will be

$$k\theta_1^{n_1}\theta_2^{n_2}\cdot\ldots\ldots\theta_0^{\Sigma n' - \Sigma n} = k'\theta'^{n'_1}_1\theta'^{n_2'}_2,\ldots. \qquad (3)$$

where k' is the rate constant of the reverse reaction and θ'_1 is the fraction of the surface occupied by the molecules A_1' etc. As a result of the equality of the rates of the forward and back reactions, the quantity of the gases on the surface will be determined by the conditions of adsorption equilibrium, which are easy to obtain according to Langmuir by setting the rate of adsorption proportional to $p_1\theta_0$ and the rate of desorption proportional to θ_1; $\theta_1 = a_1 p_1 \theta_0$ etc., where a_1 is the coefficient of adsorption.

Inserting the expressions for $\theta_1\theta_2\ldots, \theta_1'\theta_2'\ldots$ etc. in eq. (3) we notice that θ_0 drops out and we come to the law of mass action in its usual form. This deduction emphasizes the necessity of introducing the factor $\theta_0^{\Delta n}$ when the reaction is accompanied by an increase in the number of molecules.

As far as I know no conjectures have been made up to now, concerning the absolute magnitude of the constant k in the equations (2) and (2a).

Experimentally, the reaction rate is usually observed as a function of the concentrations $c_1, c_2\ldots$ or partial pressures p_1, p_2 etc. of the substances in the gas phase and not as a function of the surface concentrations. The simplest way of going over from the variables $\theta_1, \theta_2\ldots$ to the variables $p_1, p_2\ldots$ is based upon the assumption that the rate of attainment of adsorption equilibrium is large compared with the rate of the surface reaction. In this case, the connection between $\theta_1, \theta_2\ldots$ and $p_1, p_2\ldots$ is given by the well-known equations of Langmuir for adsorption equilibrium. If this assumption cannot be made, then the equation expressing the stationary state on the surface is added to equation (2) or (2a), which is the requirement that for the reactants the rate of adsorption should equal the sum of the reaction rate and the rate of desorption, for the products the rate of adsorption plus the rate of reaction should equal the rate of desorption[11], and also the equation

$$\theta_1 + \theta_2 + \ldots . + \theta_0 = 1. \qquad (4)$$

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[11] I. Langmuir, Trans. Farad. Soc, **17,** 621 (1921—1922).

The simultaneous solution of these equations gives the rate of the reaction as a function of p_1, $p_2 \ldots$ In this case, in order to estimate the velocity of the reaction, a knowledge of the rate constants of adsorption and desorption is required, as well as of the constant k in equation (2) or (2a).

There is finally the possibility of reactions as Taylor in particular emphasizes, where the rate of adsorption is the rate-determinig step.

The calculation of the speed of a process by the transition state method, is based upon the calculation of the number of molecules in the transition state (of activated complexes) using the methods of statistical mechanics. In the case of surface reactions, the activated complexes are adsorbed on the surface, and the calculation of their number may be carried out by the same methods that are used in the consideration of adsorption equilibrium. We, therefore, shall begin with the consideration of adsorption equilibrium. The methods of consideration and the formulae which we arrive at will be employed further for the calculation of the rate of surface processes.

2. Adsorption equilibrium

We shall use essentially the same method in the derivation of the equations for adsorption equilibrium, as were previously employed by the author in a thermodynamic form [12].

We proceed from the familiar expression for the Helmholtz free energy A

$$A = kT \ln Z + E_0, \tag{5}$$

where Z is the sum of states of the system

$$Z = \sum_i e^{-\frac{E_i}{kT}} \tag{6}$$

(the sum is taken over all possible states of the system; E_i is the energy of the system in the state i; E_0 is the energy of the system at $T = 0$ and depends upon the choice of the state for which the energy is taken as equal to zero).

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[12] M. Temkin, Acta Physicochimica URSS, 1, 36 (1934).

For an ideal gas consisting of N identical molecules, we have, as is well known,

$$Z = \frac{z^N}{N!}, \tag{7}$$

where z is the sum of states of the molecule

$$z = \sum_i e^{-\frac{\varepsilon_i}{kT}} \tag{8}$$

(the sum is taken over all possible states of the molecules; ε_i is the energy of the molecule in the state i), and consequently

$$A = -kTN \ln \frac{e}{N} z + N\varepsilon_0, \tag{9}$$

where $\varepsilon_0 = \frac{E_0}{N}$.

From this we obtain the chemical potential of the gas, μ. We shall calculate the chemical potential per single molecule and not per gram-molecule. In order to transform it into the ordinary quantity it is necessary to multiply μ by Avogadro's number.

Differentiation of eq. (9) gives

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{v,T} = -kT \ln \frac{z}{N} + \varepsilon_0; \tag{10}$$

z for a gas is proportional to the volume v. We introduce the partition function (the sum of states of the molecule per unit volume) with the aid of the equation:

$$F = \frac{z}{v}. \tag{11}$$

Since $\frac{N}{v} = c$ (c is the concentration of the gas, i. e. the number of molecules in cm.^{3}), we obtain

$$\mu = -kT \ln \frac{F}{c} + \varepsilon_0. \tag{12}$$

In order to calculate the chemical potential of adsorbed layer on the assumption of „simple adsorption" (see above) we consider a surface containing L elementary spaces on which N molecules are adsorbed. If the sum of states (partition function) for the adsorbed molecule is equal to F_a then the sum of states for the whole adsorbed layer is expressed in the following form:

$$Z_a = F_a^{\,N} \frac{L!}{(L-N)!\, N!}, \tag{13}$$

since every state of one molecule may be combined with every state of the second, third etc., and moreover the N molecules may be distributed on the L elementary spaces in $\frac{L!}{(L-N)!\,N!}$ ways (number of combinations of L spaces taken N at a time; the identity of the molecules is taken into account by using the number of combinations and not the number of arrangements).

We obtain for the free energy of the adsorbed layer

$$A_a = -kT \ln F_a^N \frac{L!}{(L-N)!\,N!}. \tag{14}$$

We do not write here the quantity E_0, since it may be taken equal to zero. ε_0 for the gas will then be equal to the heat of adsorption for one molecule at $T=0$. Differentiation of eq. (14) gives

$$\mu_a = \left(\frac{\partial A_a}{\partial N}\right)_{v,T} = -kT \ln F_a \frac{L-N}{N}, \tag{15}$$

since

$$\frac{d \ln N!}{dN} = \frac{\ln (N+1)! - \ln N!}{1} = \ln (N+1) \cong \ln N,$$

it being supposed that N is a very large number, and

$$\frac{d \ln (L-N)!}{dN} = -\frac{d \ln (L-N)!}{d(L-N)} \cong \ln (L-N).$$

Introducing the fraction of the surface covered

$$\theta = \frac{N}{L}$$

we obtain

$$\mu_a = -kT \ln F_a \frac{1-\theta}{\theta}. \tag{16}$$

The condition of equilibrium between the gas and the adsorbed layer is the equality of the chemical potentials

$$\mu = \mu_a.$$

Eqs. (12) and (16) give

$$\frac{\theta}{1-\theta} = \frac{F_a}{F} e^{\frac{\varepsilon_0}{kT}} c. \tag{17}$$

This equation is identical in form with the equation of the Langmuir adsorption isotherm

$$\frac{\theta}{1-\theta}=ap\ \left(\text{or } \theta=\frac{ap}{1+ap}\right), \tag{18}$$

where a is the adsorption coefficient.

Comparing equations (17) and (18) and taking into account that $p=ckT$ we find the statistical expression for a

$$a=\frac{F_a}{FkT}e^{\frac{\varepsilon_0}{kT}}. \tag{19}$$

If we neglect those changes in the motions of the atoms of the surface layer of the adsorbent that are caused by the adsorbed molecules, then the partition function may be written as a product of terms corresponding to the vibrational degrees of freedom of the adsorbed molecule

$$F_a=\prod_{i=1}^{i=3n}\left(1-e^{-\frac{h\nu_i}{kT}}\right)^{-1}.$$

The number of vibrations is equal to 3 n, where n is the number of atoms in the molecule. The vibrations are assumed to be harmonic. If the molecule may rotate freely around an axis perpendicular to the surface, then there appears in F_a the factor $\frac{2\pi(2\pi IkT)^{1/2}}{\sigma h}$, where I is the moment of inertia and σ the symmetry number and the nnmber of vibrations will be $3\,n-1$. For example, in the case of the adsorption of a monatomic gas

$$F=\frac{(2\pi mkT)^{3/2}}{h^3};\ F_a=\prod_{i=1}^{i=3}\left(1-e^{-\frac{h\nu_i}{kT}}\right)^{-1};$$

$$a=\frac{h^3}{\prod_{i=1}^{i=3}\left(1-e^{-\frac{h\nu_i}{kT}}\right)\cdot(2\pi mkT)^{3/2}kT}\,e^{\frac{\varepsilon_0}{kT}}.$$

(Cf. equation (24) in the paper by the author, cited above [12]).

The vibration frequencies of the adsorbed molecules are unknown. One may suppose, however, that they are of the same order of magnitude as the inner molecular vibration, i. e. $\left(1-e^{-\frac{h\nu}{kT}}\right)^{-1}$ differs only slightly from 1. For instance, at $T=300^\circ$ with $\nu=10^{13}$, $\left(1-e^{-\frac{h\nu}{kT}}\right)^{-1}=1.25$. The applicability of Nernst's approximate formula to adsorption equilibrium [12] serves as a confirmation of this assumption.

One can consider the adsorption of mixtures of ideal gases by the same method as used above. The chemical potential of a component of the mixture in the gas phase is equal to the corresponding value for the pure gas at the same concentration, i. e. is given by eq. (12). The number of different dispositions of the $N_1, N_2 \ldots$ etc. adsorbed molecules of the various kinds on a surface containing L elementary spaces will be equal to

$$\frac{L!}{N_1!\,N_2!\ldots(L-N_1-N_2\ldots.)!},$$

and the sum of states of the adsorbed layer will be

$$F_{a1}^{N_1}F_{a2}^{N_2}\ldots\frac{L!}{N_1!N_2!\ldots(L-N_1-N_2-\ldots)!},$$

where F_{a1} is the sum of states of the adsorbed molecule of the first kind etc.

From this we obtain for the chemical potential of a component of the mixture on the surface

$$\mu_{a1}=-kT\ln F_{a1}\frac{\theta_0}{\theta_1}. \tag{20}$$

The condition for equilibrium will be

$$\frac{\theta_1}{\theta_0}=\frac{F_{a1}}{F}e^{\frac{\varepsilon_{01}}{kT}}c \tag{21}$$

(F_1 is the distribution function of the gas molecule of the first kind etc.), or

$$\frac{\theta_1}{\theta_0}=a_1p. \tag{22}$$

Equations of the type of eq. (22) for each component, together with eq. (4), lead to the familiar formulae for the adsorption of a mixrure of gases.

3. Adsorption equilibrium when the molecule occupies two elementary spaces

According to Langmuir's concepts, the carbon monoxide molecule adsorbed on the surface of platinum occupies two elementary spaces. The ordinary structure $\overset{+}{C} \equiv \overset{-}{O}$ evidently changes into the structure $> C = O$ with two free valencies, which are joined with the two valencies of the surface atoms. It is necessary to distinguish from this case, that of adsorption accompanied by dissociation, for example the activated adsorption of H_2 on metals where according to the views of Langmuir, Taylor and others the molecule dissociates into atoms. In this case also, the molecule occupies two elementary spaces, but they may not be adjacent. It is true that in the first moment the H atoms are evidently adsorbed on neighbouring spaces, but according as equilibrium is attained, there is created a random distribution of the atoms on the surface.

Such a random distribution may come about as a result of surface migration of the atoms. Even if migration does not take place, isolated atoms must appear on a surface representing a regular plane lattice in the following way. Let us imagine four adjacent elementary spaces lying on a straight line. Let one H_2 molecule be adsorbed on the first and second space, and another on the third and fourth, the molecules being dissociated into atoms. The atoms occupying the second and third spaces may now break away from the surface in the form of an H_2 molecule, leaving isolated H atoms on the first and fourth spaces. It is evident that a mechanism of this kind will in the long run lead to a completely random covering of the surface with H atoms.

It goes without saying that the covering will be a random one only under the assumption of the absence of interaction between the adsorbed atoms.

In the case of the activated adsorption of the oxygen molecule, we may assume like Langmuir that it is adsorbed in the form of atoms, or suppose that one bond in the molecule is ruptured, and the group $-O-O-$ is united to the surface. The latter hypothesis corresponds to the peroxide theory of Bach and the viewpoint developed by him concerning the action of oxidation catalysts [13]. We may thus assume for oxygen, either adsorption of the H_2-type or of the CO-type. The same may be said about the adsorption of N_2. Although we cannot with certainty assert that the activated adsorption of H_2 and CO takes place as proposed above, we shall use for the sake of brevity the terms „adsorption of the hydrogen type“ and „adsorption of the CO type“ to denote the cases of adsorption considered, namely adsorption accompanied by dissociation and adsorption where the molecule occupies two neighbouring elementary spaces.

The consideration of adsorption equilibrium for the case of adsorption of the H_2 type may be accompanied by application of the above method, where the condition for equilibrium will be

$$\mu = 2\mu_a.$$

μ, or the chemical potential of gaseous H_2, and μ_a, or the chemical potential of adsorbed atomic hydrogen, are defined by equations (12) and (16). We arrive at the well-known equation

$$\frac{\theta}{1-\theta} = (ap)^{1/2}, \tag{23}$$

where a is defined by

$$a = \frac{F_a^2}{FkT}\, e^{\frac{\varepsilon_0}{kT}}. \tag{24}$$

This derivation, in essence, is identical with the derivation in the author's article cited above [12]. The general consideration of the condition for equilibrium in adsorption of the CO-type is rather difficult. The number of possible ways of distributing the molecules on the surface, which determines the free energy of the adsorbed layer, depends upon the kind of symmetry of the plane lattice formed by the elementary spaces. In crystals there exist four types of symmetrical plane lattices: lattices formed by rectangles, squares, rhombs and equilateral triangles [14]. Besides this there may be lattices without a plane of symmetry, consisting

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[13] A. Bach, J. Russ. Phys. Chem. Soc., **44**, apendix (1912) (Russ.).
[14] Wulf, Principles of Crystallography, Moscow, 1923 (Russ.).

of oblique-angled parallelograms. Each plane lattice may be characterised for our purposes by a number g indicating the number of elementary spaces adjacent to the given one. We term adjacent spaces those to be found at the most favorable distance for adsorption. It is assumed that spaces with other distances do not adsorb. Otherwise we should have various kinds of adsorption with various heat effects, i. e. a considerably more complex picture.

Evidently g may have the values 2, 4, 6 depending upon the symmetry of the plane lattice.

Lattices with $g = 2$, i. e. the least degree of symmetry, are equivalent to a linear disposition of the elementary spaces at equal distances. In this case it is easy to carry out the computation of the number of ways of covering the surface. Let N molecules be adsorbed on L spaces, so that the number of free spaces is equal to $(L - 2N)$, since every molecule occupies two spaces. Employing the formula for the number of permutations with repetition we find that

$$\frac{(L-N)!}{(L-2N)!\,N!}$$

various ways of covering are possible.

We obtain for the free energy of the adsorbed layer

$$A_a = -kT \ln F_a^N \frac{(L-N)!}{(L-2N)!\,N!}, \tag{25}$$

from which

$$\mu_a = -kT \ln F_a \frac{(L-2N)^2}{(L-N)\,N} \tag{26}$$

follows from the expressions given above for $\frac{d \ln N!}{dN}$ and $\frac{d \ln (L-N)!}{dN}$ and also from

$$\frac{d \ln (L-2N)!}{dN} = -2\,\frac{d \ln (L-2N)!}{d \ln (L-2N)} = -2 \ln (L-2N).$$

The number of molecules on the surface completely covered is equal to $\frac{L}{2}$, so that the fraction covered is determined by

$$\theta = \frac{2N}{L},$$

and equation (26) may be rewritten thus:

$$\mu_a = -kT \ln F_a \frac{4(1-\theta)^2}{(2-\theta)\theta}. \tag{27}$$

The condition $\mu = \mu_a$ and eqs. (12) and (27) give

$$\frac{(2-\theta)\theta}{4(1-\theta)^2} = \frac{F_a}{F} e^{\frac{\varepsilon_0}{kT}} c. \tag{28}$$

Thus we obtain the adsorption isotherm in the form

$$\frac{(2-\theta)\theta}{4(1-\theta)^2} = ap, \tag{29}$$

where a is defined by eq. (19).

The complete consideration of adsorption of the carbon monoxide type on surfaces with $g = 4$ and $g = 6$ is difficult, and we shall confine ourselves to a consideration of weak adsorption. Let N molecules be located upon L elementary spaces, and $L \gg N$.

The position of a molecule on the surface may be determined by fixing at first one elementary space and then a second one, adjacent to it. The first spaces may be occupied in $\frac{L^N}{N!}$ ways. This is seen directly and also from $\frac{L!}{(L-N)!\,N!} \cong \frac{L^N}{N!}$ if $L \gg N$.

In each case the second space may be occupied in g ways (with poor covering the molecules do not “disturb“ one another). In all we obtain $\frac{L^N}{N!} g^N$ ways of disposition, and we have

$$Z_a = F_a^N \frac{L^N}{N!} g^N.$$

We have assumed the molecule to be unsymmetrical, i. e. we have supposed the bond with the first space to be different from that with the second; otherwise we should have to divide the result by 2^N. However, we shall suppose the symmetry number of the adsorbed molecule to be included in F_a. The expression given for L_a is thus perfectly general. Further, in the same way as above we obtain the equation

$$\theta = g \frac{F_a}{F} e^{\frac{\varepsilon_0}{kF}} c. \tag{30}$$

For $\theta \ll 1$, equation (28) obviously gives eq. (30) with the particular value of $g = 2$.

4. General formulation of the kinetics of surface reactions

Let us consider in a general form the problem of determining the rate of reaction on a surface. The molecules of the initial substances may be adsorbed on the surface or be present in the gas phase. Thus we include in the consideration reactions between adjacently adsorbed molecules and those reactions which take place by impact of a molecule from the gas phase upon an adsorbed molecule.

Besides the molecules participating in the reaction, the molecules of the reaction products and of extraneous substances ("poisons") may be present on the surface.

The consideration will be based upon the simplified assumptions of the picture of "simple adsorption" (see above), and also upon the assumption of a completely random distribution of the molecules on the surface. We shall return to the discussion of this last point later.

While we assume that the reacting and other molecules occupy one elementary space each, it is necessary to assume that the activated complex may occupy several adjacent elementary spaces. For the reaction $A + B = C$, for example, taking place between molecules adsorbed on neighbouring spaces, it is necessary to regard the transition state as occupying two elementary spaces.

We shall choose a certain small interval dl along the reaction path with the top of the energy barrier in the centre of the interval, and shall regard a group of molecules as the activated complex if the point representing the configuration of this system falls within our interval dl. We may now speak of the number of activated complexes on the surface, N_t, in the same way as of the number of molecules of the first, second etc. substances, N_1, $N_2 \ldots$ etc.

Let the total number of elementary spaces be denoted by L. We shall suppose that the activated complex occupies s elementary spaces and shall denote by g the number of possible positions of the activated complex, when one of the occupied spaces is fixed. The number g depends upon the type of plane lattice formed by the elementary spaces, for example for $s = 2$, g may have the values 2, 4, 6 (see above). We shall take account of the possible symmetry of the activated complex by introducing the symmetry number into its partition function. The calculation of the number of ways of distributing the molecules and activated complexes on the surface is facilitated by the fact the N_t is a small number in comparison with L.

We distribute the activated complexes upon the surface. This can be done in

$$\frac{L^{N_t}g^{N_t}}{N_t!}$$

ways.

The adsorbed molecules may be distributed among the remaining $L-sN_t$ places in

$$\frac{(L-sN_t)!}{N_1!\,N_2!\,..(L-sN_t-N_1-N_2-\ldots.)!}$$

ways.

[sN_t evidently cannot be neglected in the factorials. For example, if $L=10^{15}$ and $sN_t=1$, then neglecting sN_t we would change $(L-sN_t)!$ 10^{15}-fold].

In all we obtain

$$\frac{L^{N_t}g^{N_t}(L-sN_t)!}{N_t!\;N_1!\;N_2!..(L-sN_t-N_1-N_2-\ldots.)!}$$

various ways of covering the surface.

We obtain for the free energy of the surface

$$A_a=-kT\ln F_t^{N_t}F_{a1}^{N_1}F_{a2}^{N_2}\ldots$$
$$\ldots\frac{L^{N_t}g^{N_t}(L-sN_t)!}{N_t!\,N_1!\,N_2!..(L-sN_t-N_1-N_2-\ldots)!}+N_t\varepsilon_{0t}, \qquad (31)$$

where ε_{0t} is the energy of the activated complex at 0°K. The energy of the adsorbed molecules at 0°K is taken as zero.

We obtain from this the chemical potential of the activated complexes

$$\mu_t=\left(\frac{\partial A}{\partial N_t}\right)_{T,v,N}=-kT\ln F_t g\frac{L}{N_t}\left(\frac{L-N_1-N_2-\ldots}{L}\right)^s+\varepsilon_{0t}$$

or $$(32)$$

$$\mu_t=-kT\ln F_t g\frac{L}{N_t}\theta_0^s+\varepsilon_{0t}$$

on differentiating the factorials as explained above and neglecting small numbers in the result.

The chemical potential of the adsorbed molecules is given by eq. (20), and for the gaseous components of the reaction, by eq. (12).

The condition for equilibrium of the activated complexes with the initial substances will be

$$\mu_t = n_1\mu_{a1} + n_2\mu_{a2} + \ldots . + r_1\mu_1 + r_2\mu_2 + \ldots ., \tag{33}$$

where μ_{a1}, $\mu_{a2}\ldots$.etc. are the chemical potentials of the substances entering the reaction from adsorbed state, μ_1, $\mu_2\ldots$etc. are those of the substances entering the reaction from the gas phase and n_1, $n_2, \ldots,$ r_1, $r_2\ldots$are the corresponding coefficients in the equation of the reaction.

Inserting the value of the chemical potentials from equations (32), (20) and (12) in eq. (33), we arrive at the equation

$$N_t = L \frac{gF_t}{F_{a1}^{n_1} F_{a2}^{n_2} \ldots F_1^{r_1} F_2^{r_2}} e^{-\frac{\varepsilon_0}{kT}} \theta_1^{n_1} \theta_2^{n_2} \ldots c_1^{r_1} c_2^{r_2} \ldots \theta_0^{s-\Sigma n} \tag{34}$$

giving the number of activated complexes. (ε_0 denotes the excess of energy of the activated complex over the energy of the initial molecules at 0°K). This number, divided by the mean life of the transition state and by 2, gives the rate of the process [2] with $\varkappa = 1$. The task amounts to excluding from the partition function of the transition state in (34) the factor which refers to the reaction path, after which one obtains the quantity F_t', and the expression must be multiplied by $\frac{kT}{h}$ equal to half the partition function for the reaction path divided by the mean life of the transition state [1]. Introducing the transmission coefficient $\varkappa$ we obtain for the velocity of the process, the expression

$$\omega = \varkappa L \frac{gF_t'}{F} \frac{kT}{h} e^{-\frac{\varepsilon_0}{kT}} \theta_1^{n_1} \theta_2^{n_2} \ldots c_1^{r_1} c_2^{r_2} \ldots \theta_0^{s-\Sigma n}, \tag{35}$$

where, for the sake of brevity, the notation $F = F_{a1}^{n_1} F_{a2}^{n_2} \ldots F_1^{r_1} F_2^{r_2}$ is introduced.

If only adsorbed molecules participate in the reaction, then this equation conforms to eqs. (2) and (2a), in case the number of spaces occupied by the activated complex s is equal to the number of molecules of the initial substances or the number of molecules of the products, depending upon which of these numbers is greater. Such an assumption is quite natural but not the only one possible.

As we have already pointed out, eq. (35) generally speaking implies a random distribution of the molecules on the surface. This random distribution may be realized as a result of the surface mobility of the molecules or as a result of exchange with the gas phase. Such a restriction is not needed for unimolecular reactions, but a bimolecular reaction requires a continuous renewal of pairs of molecules adsorbed on neighbouring elementary spaces.

A random distribution will always be obtained irrespective of the surface mobility, if the rate of establishment of adsorption equilibrium considerably exceeds the rate of the reaction.

The substances on the surface in this case are present in an equilibrium amount with respect to the gas phase, which makes it possible to express eq. (35) in another form. Substituting the values of θ_1, θ_2 etc. from eq. (21) into (35) we obtain

$$\omega = \varkappa L \frac{gF'_t}{F} \frac{kT}{h} e^{-\frac{\varepsilon_0}{kT}} c_1^{n_1} c_2^{n_2} \ldots \theta_0^s \tag{36}$$

or

$$\omega = \varkappa L \frac{gF'_t}{F(kT)^{\Sigma n}} \frac{kT}{h} e^{-\frac{\varepsilon_0}{kT}} p_1^{n_1} p_2^{n_2} \ldots \theta_0^s \,. \tag{36a}$$

F in eqs. (36) and (36a), in contrast with eq. (35), denotes the product of the partition functions for the initial substances in the gaseous state, and ε_0 is the excess in the energy of the transition state over the energy of the initial substances in the gaseous state. We could arrive at eq. (36) directly by setting the chemical potential of the transition state equal to the sum of the chemical potentials of the initial substances in the gaseous state.

In case the amounts adsorbed correspond to the equilibrium, there is obviously no sense in distinguishing between the substances entering into reaction after having been preliminarily adsorbed and the substances directly entering into the reaction from the gas phase.

Equation (36a) is especially convenient if all the substances are so weakly adsorbed that we may put $\theta_0 = 1$. We then directly obtain the expression for the rate in terms of the partial pressures in the gas phase, and the quantity ε_0 is then the so-called apparent activation energy at 0° K.

The general expression for θ_0 may be readily obtained from eqs. (22) and (4):

$$\theta_0 = \frac{1}{1 + a_1 p_1 + a_2 p_2 + \dots}. \tag{37}$$

In using eqs. (35), (36) and (37) for an approximate estimation of the absolute rate of the reaction in case the potential surface for the reaction is unknown, one may regard $F_t^{'}$ and F_{a1}, F_{a2} etc. as equal to unity since they correspond to vibrational degrees of freedom. At the same time, the factors in F_1, F_2 etc., corresponding to vibrational degrees of freedom, will also be supposed to be 1, which partly compensates the error. After this the calculation is not difficult. We are in a more favorable situation in this respect than in the case of homogeneous reactions, since the application of eq. (1) requires a knowledge of the moments of inertia of the activated complex.

We shall consider as an example of such a calculation, the reaction involving the decomposition of phosphine in a glass vessel. Van't-Hoff[15] found that the course of this reaction at 440° C accurately follows the first order equation. Kooij[16], using the apparatus of Van't Hoff, measured the rate of this reaction at four temperatures in the interval 310 — 512° C and expressed his results through the equation

$$\log K = -\frac{3595}{T} + 2.4884 \tag{38}$$

(K is the first order constant; the time is expressed in hours).

Trautz and Bhandankar[17] showed that the reaction which Van't-Hoff and Kooij had observed took place on the walls of the vessel and not in the gas phase. These authors thought that at higher temperatures they succeeded in observing the homogeneous

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[15] Van't Hoff, Etudes de dynamique chimique.

[16] Kooij, Z. physik. Chem., **12**, 155 (1893).

[17] Trautz a. Bhandankar, Z. anorg. Chem., **106**, 95 (1919).

reaction. Hinshelwood and Topley[18] showed, however, that at high temperatures also, only the surface reaction is observed. Unfortunately, Van't Hoff and Kooij do not indicate the volume and surface of the vessel they used. This is not surprising since they regarded the reaction as homogeneous[19].

Judging from Figs. 11 and 13 in Van't Hoff's book, the vessels were tubes of 16 mm. in diameter and 60 mm. in length. This corresponds to a volume of 12 cm.^{3} and a surface of 34 cm.^{2}. Since the number of molecules in the volume v is determined by the equation $N = \frac{pv}{kT}$, it follows that $\omega = -\frac{dN}{dt} = -\frac{v}{kT}\frac{dp}{dt}$, and we obtain for the rate of the reaction, expressed in terms of the number of molecules decomposing on 1 cm.^{2} per second, the equation

$$\omega = \frac{10^{2.4884} \times 12}{\underbrace{3600}_{\text{Sek.}} \times 34 \times kT} e^{-\frac{\varepsilon'}{kT}} p = \frac{2.2 \times 10^{14}}{T} e^{-\frac{\varepsilon'}{kT}} p, \qquad (39)$$

where $\frac{\varepsilon'}{k} = 3595$ and p is the pressure in dynes per cm.^{2}.

Introducing into equation (36a) the expressions for the partition functions of the translational and rotational degrees of freedom and supposing that the partition function for the vibrations is equal to 1, we obtain with $\varkappa = 1$

$$\omega = \frac{gL \frac{1}{\sigma^*} \frac{kT}{h}}{\frac{(2\pi mkT)^{3/2}}{h^3} \frac{8\pi^2 (8\pi^3 I_A I_B I_C)^{1/2} (kT)^{3/2}}{\sigma h^3} kT} e^{-\frac{\varepsilon_0}{kT}} p, \qquad (40)$$

where m is the mass of the molecule; I_A, I_B and I_C are the principal moments of inertia; σ is the symmetry number; σ^* is the corresponding quantity for the activated complex.

It is necessary to take into account, upon comparison of equation (39) with (40), that the quantities ε_0 and ε', and the pre-ex-

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[18] Hinshelwood a. Topley, J. Chem. Soc., **125**, 393 (1924).

[19] It is more surprising that data of this kind are ordinarily lacking in the papers of the authors who knew that the reaction they studied proceeded on the walls of the vessel. For a long time no significance was attached to the absolute magnitude of the rate of surface reactions, and only the dependence of the rate upon the concentration and the temperature was considered of interest.

ponential factors in these equations do not completely agree. Extending to the present case the ideas expressed by Langmuir[20] in discussing the dependence of the vapor pressure upon the temperature, we can say that the dependence of k upon T may be given with equal success by a formula of the type

$$k = Be^{-\frac{\varepsilon}{kT}} \tag{41}$$

and

$$k = B' T^{\gamma} e^{-\frac{\varepsilon'}{kT}} \tag{42}$$

if there are the following relations between the quantities in these formulae:

$$B = B' T_M e^{\gamma} \tag{43}$$

and

$$\varepsilon = \varepsilon' + \gamma k T_M, \tag{44}$$

where T_M is the mean temperature of the interval to which eqs. (41) and (42) are applied.

Thus instead of eq. (39) we can write ($\gamma = -1$, $T_M = 684$)

$$\omega = 1.2 \times 10^{11} e^{-\frac{\varepsilon}{kT}} p. \tag{45}$$

In eq. (40) $\gamma = -3$ so that, for comparison with eq. (45), we have to divide the pre-exponential factor by e^3. We take $L = 10^{15}$ since we are only interested in the order of magnitude. Since the reaction leads to the splitting of the molecule into unequal parts it is natural to suppose that the transition state occupies two elementary spaces and is unsymmetrical, so that $\sigma^* = 1$. For g we take the average value 4.

The quantities I_A and I_B are known: $I_A = I_B = 0.62 \times 10^{-39}$ g cm.^{2}. I_C is set equal to 10^{-39} g cm.^{2} since it must be greater than I_A and I_B (for ammonia $I_A = I_B = 0.28 \times 10^{-39}$ and $I_C = 0.43 \times 10^{-39}$ g cm.^{2} [21]).

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[20] I. Langmuir, J. Am. Chem. Soc., **54**, 2798 (1932).

[21] Kronig, The optical basis of the theory of valency, Cambridge 1935.

$\sigma = 3.$ $T_M = 684$, and from eq. (40) we obtain

$$\omega = 0.5 \times 10^{11} e^{-\frac{\varepsilon}{kT}} p, \tag{46}$$

i. e. the result is close in the order of magnitude to the value of k in eq. (45). If we took into account that the true surface may exceed the geometrical surface by a factor of several-fold we would have obtained a complete agreement between the calculated and experimental reaction rates.

Hinshelwood, in connection with the calculation of the absolute magnitude of the rate of the homogeneous reaction $2HJ = 2H_2 + J_2$ by means of the calculation of the number of collisions, says: "The calculation in no way depends upon interpolation but is absolute, there being nothing in the form of the equations which constrains log K to lie between fixed values. It might have almost any value, and an essentially wrong theory could lead to results tens of millions of times too large or to small. Hence an even less exact agreement than that obtained here would have been satisfactory from the point of view of ascertaining the general correctness of the assumptions made".

It seems to me that these words are entirely applicable to the calculation of the absolute value of the rate of decomposition of PH_3 on glass, carried out above. I should like also to point out that in the calculation of the absolute rate of this reaction we need to know only the value of the apparent activation energy, and are not interested at all in the so-called true activation energy.

5. The rate of activated adsorption

We shall here consider only the initial rate of adsorption, i. e. the rate of adsorption on a free surface. Below we shall revert to the question of the dependence of the rate of adsorption upon the surface covered. We shall begin with the derivation of the familiar formula for the number of impacts of gas molecules on 1 cm.^{2} of surface in 1 sec., since this derivation makes it possible to examine the peculiarity of the problem of the rate of activated adsorption.

In the calculation of the number of impacts, the gas molecules are considered to be elastic spheres, their rotational state is assumed to be unchanged upon impact and therefore may be ignored. The surface is considered to be an ideal plane while any forces of interaction between the surface and the molecules are absent. The coordinate corresponding to the reaction path will be normal to the surface, and the transition state will be the moment when the distance between the surface of the sphere and the plane is infinitely small. The two components of motion, parallel to the plane, remain unchanged and preserve the character of free translational motion. Since the partition function for translational motion per unit length is equal to $\frac{(2\pi mkT)^{1/2}}{h}$, equation (1) gives ($\varkappa = 1$, $\varepsilon_0 = 0$)

$$k = \frac{\frac{2\pi mkT}{h^2}}{\frac{(2\pi mkT)^{3/2}}{h^3}} \frac{kT}{h} = \frac{kT}{(2\pi mkT)^{1/2}} .$$

Multiplying k by the concentration of the gas c we obtain the number of impacts

$$M = \frac{ckT}{(2\pi mkT)^{1/2}} = \frac{p}{(2\pi mkT)^{1/2}} , \qquad (47)$$

where M is the number of impacts on 1 cm.^{2} for 1 sec. at the pressure p. The result coincides with the familiar formula of the kinetic theory of gases but is obtained in a considerably briefer way. If we assumed the existence of repulsive forces acting normally to the surface and creating an energy barrier, so that ε_0 would be different from zero, and preserved the other assumptions, we should obtain for the velocity of adsorption the expression

$$\omega = \frac{p}{(2\pi mkT)^{1/2}} e^{-\frac{\varepsilon_0}{kT}} = Me^{-\frac{\varepsilon_0}{kT}} . \qquad (48)$$

The conception of free motion of the adsorbed molecule along the surface corresponds to treating the adsorbed layer as a two-dimensional gas. In reality, as is assumed in the Langmuir theory of adsorption, the adsorbed molecules do not move freely along the surface, but vibrate about definite equilibrium positions, only rarely jumping over to another position. It is obvious that under these conditions eq. (48) ceases to be valid.

In order to calculate the rate of adsorption in conformity with the theory of Langmuir we must employ eq. (35). We obtain

$$\omega = \varkappa L \, \frac{gF_t^{\neq}}{F} \, \frac{kT}{h} \, e^{-\frac{\varepsilon_0}{kT}} \, c, \tag{49}$$

i. e. the same equation as for unimolecular reactions on practically free surface.

Activated adsorption is ordinarily observed for diatomic gases: H_2, CO, O_2, N_2. Independently of whether we observe adsorption of the type of H_2 on Pt or of the type of CO on Pt, the transition state for adsorption occupies two elementary spaces, and the difference between these two types of adsorption affects only the dependence of the velocity upon the extent of covering of the surface and not upon the initial velocity of adsorption.

Applying eq. (49) to the adsorption of diatomic molecules, we obtain, upon using the expressions for the partition functions of the translational, rotational and vibrational degrees of freedom,

$$\omega = \varkappa L \, \frac{g\sigma \prod\limits_{i=1}^{i=5} \left(1 - e^{-\frac{h\nu_i^*}{kT}}\right)^{-1} \dfrac{kT}{h}}{\sigma^* \, \dfrac{(2\pi mkT)^{3/2}}{h^3} \left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1} \dfrac{8\pi^2 IkT}{h^2}} \, e^{-\frac{\varepsilon_0}{kT}} \cdot c \tag{50}$$

In this equation m is the mass; I, the moment of inertia; ν, the vibrational frequency and σ, the symmetry number. The quantities referring to the transition state are marked with asterisks. Assuming that $\varkappa = 1$, and the frequencies are so great that $\left(1 - e^{-\frac{h\nu}{kT}}\right) = 1$, we obtain for the velocity of adsorption

$$\omega = \frac{Lg\sigma h^4}{\sigma^* \, (2\pi mkT)^{3/2} \, 8\pi^2 IkT} \, e^{-\frac{\varepsilon_0}{kT}} \, p. \tag{51}$$

Let us compare formulae (51) and (48). For this purpose we denote by α the ratio of the rate of adsorption according to eq. (51) and the value predicted by eq. (48). Introducing the correction according to eq. (43), we obtain

$$\alpha = \frac{Lg\sigma h^4}{16\pi^3 \sigma^* \, (kT_M)^2 \, Ie^2 m} \, . \tag{52}$$

As an example let us consider the activated adsorption of hydrogen at room temperature.

$I = 0.46 \times 10^{-40}$, $\sigma = \sigma^* = 2$. We take $L = 10^{15}$, $T_M = 300$, $g = 6$ (the most common type of faces for metals). We find that $\alpha = 2 \times 10^{-2}$.

For the adsorption of oxygen under the same conditions we find ($I = 1.9 \times 10^{-39}$) $\alpha = 1.8 \times 10^{-5}$. Thus α may considerably differ from unity.

The values which we have calculated are the lower limits for α, since if the ν^* are small α will be nearer to 1.

Considerably smaller values of α have been found in the case of adsorption on porous adsorbents with a strongly developed inner surface, while on a smooth surface a value of the above order of magnitude was observed (the rate of adsorption of H_2 on Ni from the measurements of Leypunsky [9]). In the case of porous catalysts, the rate of adsorption may evidently be determined by the velocity of diffusion on to the inner surface (Ward [22]).

The rate of a reaction occurring upon collision of a molecule from the gas phase with the layer of adsorbed molecules on the surface of the catalyst is determined by the same equations as for the rate of activated adsorption. Here, also, upon comparing the pre-exponential factor in the expression for the rate of reaction with the number of impacts upon the surface, we arrive at values of α considerably differing from 1.

The reaction between nitric oxyde and oxygen on the surface of glass, which was studied by the author and Pyzhov [23] at low temperatures (79° K — 88° K), serves as an example. We came to the conclusion that the reaction takes place by collision of oxygen molecules with adsorbed NO molecules. Although the true activation energy is zero, only one in 10^4 collisions leads to reaction. The value of α for O_2 (1.8×10^{-5}) given above corresponds to $T_M = 300$. At $T_M = 84$, α is 13 times larger as is easily seen from eq. (52), i. e. of the order of 10^{-4}.

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[22] Ward, Proc. Roy Soc., **A 133,** 522 (1931).

[23] M. Temkin a. Pyzhow, Acta Physicochimica URSS, **2,** 473 (1935).

Another example is the reaction $H_2 + CO_2 = CO + H_2O$ on the surface of platinum. The author and Michailova[24] pointed out the errors in the technique of the preceding investigators of this reaction (Hinshelwood and Pritchard, Srikantan) and, upon the basis of the investigation of the kinetics with an improved technique, concluded that the reaction takes place by means of a collision of a CO_2 molecule from the gas phase with an adsorbed H_2 molecule. In the temperature range studied, the rate of the reaction was determined by the rate of evaporation of CO from the surface.

This reaction was later studied by Schwab[25], who evidently was not familiar with our work, since he at first repeated the same errors in the technique as Hinshelwood and Pritchard and Srikantan and only later resorted to a method coinciding with that used by us. He also came to the conclusion that the reaction takes place by collision of a CO_2 molecule with the film of the adsorbed hydrogen. Since Schwab studied the reaction at low pressures he was able to measure its velocity in the high temperature region under conditions where the surface is free of CO. He found that although the reaction proceeds without any energy of activation, only 1 collision in 10^4 of CO_2 upon the surface covered with hydrogen leads to reaction. Schwab concluded from this that only a 10^{-4}-th part of the surface is catalytically active. It follows from the above considerations that there is no basis for such a conclusion.

6. Dependence of the velocity of activated adsorption upon the amount adsorbed. Adsorption pseudo-equilibria

If the adsorbed molecule occupies one elementary space, then as eq. (35) shows, the rate of adsorption is simply proportional to θ_0. The relationships are more complicated in the cases of adsorption accompanied by dissociation (adsorption of the type of H_2 on Pt) and in the case when the molecule occupies two elementary spaces (adsorption of the type of CO on Pt). For adsorption of the hydrogen type, we again arrive at a simple result if we

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[24] M. Temkin a. Michailova, Acta Physicochimica URSS, **2**, 9 (1935).

[25] Schwab a. Naicher, Z. Elektrochem., **42**, 670 (1936).

assume that the velocity of surface diffusion is very large in comparison with the velocity of adsorption. Then we can again employ eq. (35) which shows that the dependence of the rate upon the amount adsorbed is expressed by the factor θ_0^2.

For adsorption of the CO type, eq. (35) cannot be applied directly, since it was derived upon the assumption that the molecules on the surface occupy one elementary space each and that only the activated complexes can occupy *s* elementary spaces. However, here the assumption of a large velocity of surface diffusion greatly simplifies the problem. It is easy to obtain for a surface with $g=2$, a rate equation corresponding to the equilibrium equation (eq. 29). Since the rate of desorption is obviously proportional to θ, the rate of adsorption must be proportional to $\frac{4(1-\theta)^2}{2-\theta}$. This factor should be introduced into eq. (40) in place of *g*. This result may also be easily obtained by considering the joint adsorption of ordinary molecules and molecules in the transition state. Similar results may be expected for other values of *g*.

Let us qualitatively consider the other limiting case, when surface diffusion is absent, for adsorption of the H_2 type. Let the equilibrium correspond to a small extent of covering of the surface; for example $\theta=0.01$. At first the atoms will be distributed in pairs, i. e. we shall have adsorption of the CO type; however, in such a way only a small number of molecules can be adsorbed. In fact, while for adsorption of the H_2 type equilibrium is determined by the equation

$$\theta=\sqrt{ap}, \quad (\theta\ll 1),$$

for adsorption of the CO type it is determined by the equation

$$\theta=gap, \quad (\theta\ll 1),$$

and *a* is identical in both equations. If $\sqrt{ap}=0.01$, then $gap=$ $=0.0006$ (with $g=6$). Thus after a comparatively rapid adsorption of a small quantity of gas, i. e. about 6% of the equilibrium amount in the example considered, there takes place a slower process of the formation of isolated atoms by the mechanism described above (Section 3). Since this process requires the adsorption of two adjacent molecules, the velocity of adsorption in a definite region may turn out to be proportional to the square of the concentration in the gas phase.

Now let us suppose that surface diffusion is absent as before, but the equilibrium amount corresponds to complete covering, i. e. desorption of the molecules practically does not take place. In this case the distinction between adsorption of the H_2 and CO types disappears. The true equilibrium, that is complete covering of the surface, is not reached at all, since the free elementary spaces which turn out to be isolated, all the adjacent ones being occupied, will be lost for adsorption. It is interesting to calculate the probable number of such free spaces. The calculation is easy to carry out for surfaces with $g = 2$. As has already been pointed out this is equivalent to spaces arranged along a straight line. One may imagine the case where the molecules accidentally fill up all the spaces. On the other hand there is the possibility that there will be a free space after every molecule so that $\frac{1}{3}$ of the surface will remain free. Both these cases, however, are very unlikely with a large number of spaces.

We wish to find the most probable covering, i. e. that which can be attained in the largest number of ways. Let 2 N out of L spaces be occupied by N molecules, in pairs, so that the free spaces are isolated. All the possible ways of obtaining such a type of covering may be divided into two groups: (a) the first space is occupied and (b) the first space is free. In order to calculate the possible ways of covering of the group (a) we mentally join every free space to the preceding pair of occupied spaces. Thus we obtain elements of two kinds — combinations of three spaces in each of which the first two are occupied and the third is free, $L - 2N$ in number, and the remaining pairs of occupied spaces, $N - (L - 2N)$ or $3N - L$ in number. The total number of elements is N. Applying the formula for the number of permutations with repetition we obtain for the number of different ways of covering of group (a):

$$W_a = \frac{N!}{(L-2N)!\,(3N-L)!}\,.$$

We omit the first space in calculating the number of coverings belonging to group (b). We then obtain again the case already considered with the distinction that we have $L-1$ spaces instead of L.

We obtain for the number of ways of covering

$$W_b = \frac{N!}{(L-2N-1)!\,(3N-L+1)!} = \frac{N!}{(L-2N)!\,(3N-L)!} \times \frac{L-2N}{3N-L+1}.$$

The total number of possibilities W will be the sum of W_a and W_b.

$$W = W_a + W_b = \frac{N!}{(L-2N)!\,(3N-L)!} \times \left(1 + \frac{L-2N}{3N-L+1}\right) =$$

$$= \frac{N!}{(L-2N)!\,(3N-L)!} \times \frac{N+1}{3N-L+1} = \frac{(N+1)!}{(L-2N)!\,(3N-L+1)!}.$$

We shall suppose that the number N is the most probable one if it corresponds to the maximum W. Instead of seeking the maximum of W, we shall seek the maximum of $\ln W$ by differentiating the logarithms of the factorials as has been done above (neglecting the terms which are small in comparison with L and N in the result). We obtain

$$\frac{d \ln W}{dN} = \ln \frac{N(L-2N)^2}{(3N-L)^3} = 0,$$

or introducing $\theta = \frac{2N}{L}$,

$$\frac{\frac{1}{2}\theta\,(1-\theta)^2}{\left(\frac{3}{2}\theta - 1\right)^3} = 1.$$

A root of this cubic equation is $\theta = 0.82$. Similar results may be expected for other values of g.

Thus, in the above case of adsorption, the surface does not become completely covered but only to 82% or near to this. If the evaporation of the molecules (or surface diffusion), although taking place very seldom, is not completely absent, then the whole surface gradually becomes covered. We may observe that 82% of the total quantity of adsorbed gas is adsorbed rapidly and the remaining 18%, slowly. If we now carry out the desorption of such a surface covered with a gas by placing it into a continuously maintained vacuum at such a high temperature that the evaporation of the molecules from the surface will proceed with a considerable velocity, then the behaviour will be different for adsorption of the H_2 type and the CO type. In the case of CO all the molecules will evaporate; in the case of H_2 the atoms will break away in pairs in the form of molecules, leaving isolated atoms which, with the absence of mobility along the surface, will not be able to be desorbed. It is easy to see that upon desorption from a completely covered surface, exactly the same number of atoms will remain as there remained free places upon adsorption: i. e. 18% with $g=2$.

In observing these phenomena it is easy to come to the erroneous conclusion of the existence of two kinds of adsorption of H_2 on two kinds of elementary spaces. A large portion of the gas is adsorbed rapidly and is removed by pumping off at high temperatures; a portion of the gas is adsorbed slowly and is not removed by pumping off.

Analogous phenomena may also be observed in the case when the equilibrium amount of H_2 on the surface is small. Here only a small number of atoms situated next to one another will be removed upon pumping off, and the isolated atoms will not be pumped off. Here also, the same amount of gas will be pumped off as was adsorbed rapidly (see above).

The peculiarity of these cases of "irreversible" adsorption is that the hydrogen atoms cannot be desorbed in vacuum, but if the gas phase contains some H_2, then the equilibrium amount of atoms on the surface will be established as a result of the mechanism described in section 3, and it may be arbitrarily close to zero if the temperature is high enough. Thus, gaseous hydrogen may act as if it catalyses the desorption of hydrogen from the surface. It is evident that the kinetics of activated adsorption become still more complicated if the rate of surface diffusion is comparable with the rate of adsorption.

Enough has been said to illustrate the considerable complexity of the phenomena which determine the kinetics of activated adsorption and to explain the failure of the numerous attempts to find a theoretical basis for the equations expressing these kinetics. One should keep in mind that we have confined ourselves to the consideration of the simplest picture of a plane uniform surface. The possible non-homogeneity of the surface, diffusion to the interior of the metal and along the grain boundaries on to the surface inaccessible to direct molecular bombardment complicate the phenomena still further.

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