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Application of the Theory of Absolute Reaction Rates to Heterogeneous Processes II. Chemical Reactions on Surfaces

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adsorbed poison, however, ΔF_p^0 will have a large negative value and the rate of adsorption of the gas will be markedly decreased.

The rate of desorption of gas from a poisoned surface is still given by Eq. (21), and so from this and Eq. (48), it follows that

$$c_a = L \frac{c_g}{c_{gp}} \cdot \frac{F_{gp} f_a}{F_g f_{ap}} e^{(\epsilon - \epsilon_p)/kT},$$
(51)

where ϵ , as before, is $\epsilon_2 - \epsilon_1$, the heat of adsorption of the gas.

By utilizing the methods developed in this and the succeeding paper, equations analogous to (48) and (51) can be derived for various types of adsorption, e.g., involving dual sites or dissociation, of both gas and poison; an illustration is provided in Part II by the treatment of the decomposition of ammonia, adsorbed on a dual site, on a surface poisoned by hydrogen in the form of atoms.

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Application of the Theory of Absolute Reaction Rates to Heterogeneous Processes

II. Chemical Reactions on Surfaces

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The method developed in the preceding paper is used to derive equations for the rates of unimolecular and bimolecular heterogeneous gas reactions under various conditions of surface coverage by either reactants or poisons. The resulting equations are of the same form as those previously deduced by Langmuir and others, but they are more explicit; provided the activation energy is known they can be utilized to calculate rates of surface reactions which are in good agreement with the observed values. In the case of the dissociation of hydrogen on a tungsten surface, the simple assumption that the activated state consists of hydrogen atoms permits the absolute rate of the reaction to be calculated with an accuracy which is at least as good as that attained by direct experimental measurement. The factors responsible for the difference in rates of the same reaction taking place homogeneously or heterogeneously are considered; it is shown that adsorption of the activated complex lowers the over-all activation energy, and this has the most important influence in favoring the surface reaction. If one of the products, or any other substance acting as a poison, is strongly adsorbed, the effective activation energy is increased, but there is some compensation resulting from the increase of entropy accompanying the desorption of the poison.

INTRODUCTION

FROM the point of view of the theory of absolute reaction rates a chemical reaction taking place on a surface is formally the same as an adsorption, the initial state being a molecule, or molecules, in the gas phase while the activated state is an adsorbed molecular species. The question, frequently discussed, as to whether the adsorption process or the reaction on the surface is slow, and hence rate determining, is for present purposes of no importance, since the essential point is the equilibrium between reactants and the activated complex, whatever the latter may be. Equations for the rates of surface reactions were derived by I. Langmuir and others¹ from kinetic considerations, and it will be shown that analogous, but more explicit, equations may be obtained by using the method described in the preceding paper (Part I) of regarding the surface

¹I. Langmuir, Trans. Faraday Soc. 17, 621 (1922); C. N. Hinshelwood, *Kinetics of Chemical Change* (Oxford University Press, 1926, p. 145; 1940, p. 187); cf. H. S. Taylor, *Treatise on Physical Chemistry* (Van Nostrand Company, New York, 1931), p. 1074.

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as one of the reactants. By means of these equations the rates of a number of heterogeneous gas reactions have been calculated and found to be in agreement with the experimental values. For present purposes it is convenient to consider various reactions according to the number of molecules, *viz.*, one or two, involved in the chemical change.

UNIMOLECULAR REACTIONS

Suppose the reaction involves one molecule of the gaseous reactant A, and S represents the active center on which reaction occurs. The activated complex consists of an adsorbed molecule which has acquired the appropriate amount of energy and the proper configuration : the equilibrium between initial and activated states may be written as

$$A+S \rightleftharpoons (A-S)^{\ddagger} \rightarrow \text{products},$$

and hence

$$\frac{c^{\mp}}{c_{g}c_{s}} = \frac{f_{\pm}}{F_{g}f_{s}} e^{-\epsilon_{s}/kT},$$
(1)

where ϵ_0 is the energy of activation per molecule at 0°K, and the other symbols have the same significance as in the preceding paper. The rate of reaction according to the theory of absolute reaction rates is then

$$v = c_g c_s \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g f_s} e^{-\epsilon_0/kT}.$$
 (2)

It may be noted that this expression is formally identical with Eq. (8) of Part I for the rate of adsorption; the activated states are, however, different in the two cases, although since both consist of immobile molecules attached to the surface their partition functions will be of the order of unity, in each case, at ordinary temperatures.

First-order kinetics

The application of Eq. (2) may be considered under two sets of conditions. In the first place, if the surface is sparsely covered by adsorbed molecules, c_s , the concentration of bare sites on the surface, is practically constant and is almost identical with the number of sites per sq. cm of completely bare surface. In these circumstances c_s in Eq. (2) may be taken as constant, and the rate of reaction, for a given surface, is seen to be directly proportional to the concentration of the reacting material in the gas phase: the process is thus kinetically of the first order. Numerous examples of this type of behavior are known.

Introducing the expressions for the partition functions into Eq. (2), it follows that the rate equation for a unimolecular, first-order, reaction involving a diatomic molecule is

$$v = c_g c_s \frac{\sigma}{\sigma_{\pm}} \cdot \frac{\frac{1}{2} s h^4}{8\pi^2 I (2\pi m k T)^{\frac{3}{2}}} e^{-\epsilon_0 / k T}, \qquad (3)$$

where s is the total number of possible sites adjacent to any reaction center, σ and σ_{\pm} are the symmetry numbers of the molecules of reactant and of activated complex, respectively, and I and m are the moment of inertia and mass of the reacting molecule. For a nonlinear polyatomic molecule, the rate is

$$v = c_{g}c_{s}\frac{\sigma}{\sigma_{\pm}} \cdot \frac{\frac{1}{2}sh^{5}}{8\pi^{2}(8\pi^{3}ABC)^{1/2}(2\pi m)^{3/2}(kT)^{5/2}}e^{-\epsilon_{0}/kT},$$
(4)

where A, B and C are the three moments of inertia of the reactant. In both these equations c_s is the number of reaction sites per sq. cm of surface, and the factor $\frac{1}{2}s$ is introduced when the reacting molecules are attached to two sites in the activated state. Using known, or reasonable, values for the moments of inertia and taking sto be 4 in each case, the specific reaction rates for the surface decomposition of phosphine,² hydrogen iodide³ and nitrous oxide⁴ have been evaluated, the assumption being made that in each case the surface is smooth and sparsely covered, so that there are about 10¹⁵ individual sites per sq. cm. In Table I the calculated re-

 TABLE I. Observed and calculated first-order surface reaction rates.

			SPECIFIC REACTION RATES		
DECOMPOSI- TION OF:	SURFACE	TEMPERA- TURE	Obs.	Calc.	
PH3 HI N2O	Glass Platinum Gold	684°K 836° 1211°	$\begin{array}{r} 4.7 \times 10^{-7} \\ 1.0 \times 10^{-3} \\ 12.3 \times 10^{-5} \end{array}$	2.2×10^{-8} 1.2×10^{-3} 3.4×10^{-6}	

² J. H. van't Hoff and D. M. Kooij, Zeits. f. physik. Chemie 12 (1893); cf. M. Temkin, Acta Physicochimica U. R. S. S. 8, 141 (1938).

³ C. N. Hinshelwood and R. E. Burk, J. Chem. Soc. 127, 2896 (1925).

⁴C. N. Hinshelwood and C. R. Prichard, Proc. Roy. Soc. A108, 211 (1925). sults are compared with those observed, which are for relatively even surfaces, the values given being the ordinary first-order rate constants which refer to the particular amount of surface used in the experiment. Although the calculated and observed rates are in satisfactory agreement, it will be noted that the former are somewhat too small for the decomposition of phosphine and nitrous oxide. This may be due partly to the roughness of the surface, which would make the number of reaction centers greater than the value employed, and partly to the fact that there is some freedom of movement in the activated state. By taking the partition function for the latter to be unity it is assumed that there is no movement of any kind in the activated state; with relatively complex molecules such as phosphine and nitrous oxide rotation or libration in the activated state may well be appreciable and the inclusion of the appropriate contribution to the partition function would increase the calculated reaction rates.

Zero-order kinetics

When the surface is covered by adsorbed molecules to an appreciable extent, the value of c_s varies with the pressure of the gas, and the behavior to be expected is apparent from a combination of Eq. (2) and the adsorption isotherm; substituting the following value for $c_{g}c_{s}$ obtained from Eq. (23) of Part I, viz.,

$$c_{g}c_{s} = c_{a}(F_{g}f_{s}/f_{a})e^{-\epsilon/kT}$$

$$\tag{5}$$

in (2), it follows that

$$v = c_a \frac{kT}{h} \cdot \frac{f_{\pm}}{f_a} e^{-(\epsilon_0 + \epsilon)/kT}, \qquad (6)$$

where ϵ is the heat evolved in the adsorption of one molecule of reactant. If the surface is almost completely covered by adsorbed molecules, c_a may be taken as constant, and the rate of reaction as given by Eq. (6) is seen to be virtually independent of the pressure of the reactant: the process is then said to obey zero-order kinetics. It will be apparent that Eq. (6) treats the reaction from the standpoint of adsorbed molecules, instead of gas molecules, as the initial reactant: the "surface activation energy," i.e., the differ-

TABLE II. Observed and calculated zero-order surface reaction rates

DECOMPO- SITION OF:	SURFACE	E KCAL.	Т	k _{OBS}	k _{CALC}
NH3 ⁵ NH3 ⁶ NH3 ⁷ H1 ⁸	W W Mo Au	38 41.5 53.2 25.0	904°K 1316 1228 978	$\begin{array}{r} 4 \times 10^{17} \\ 2 \times 10^{19} \\ 5 - 20 \times 10^{18} \\ 5.2 \times 10^{22} \end{array}$	$\begin{array}{c} 8.0 \times 10^{18} \\ 3.4 \times 10^{21} \\ 8.5 \times 10^{18} \\ 1.6 \times 10^{17} \end{array}$

ence in energy between the activated state and the adsorbed reactants, is $\epsilon_0 + \epsilon$.

Since both f_{\pm} and f_a may be taken as unity, it follows that (6) may be written as

$$v = c_a (kT/h) e^{-E/RT}, \qquad (7)$$

where E is the observed activation energy per mole. An equation of the same form as (7), with a frequency factor assumed to be 10^{12} per sec., in place of kT/h, was proposed from general considerations by Toplev.¹⁰

When the surface is almost entirely covered, c_a is equal to the number of active centers per sq. cm of surface, which may be taken as 10¹⁵. In Table II are given a number of calculated and observed rate constants expressed as molecules per sq. cm per second, for zero-order reactions calculated from (7), making use of the data collected by Topley. The agreement is seen to be satisfactory except for the decomposition of hydrogen iodide on gold; the discrepancy may be due to the adsorption of hydrogen on the surface, for this would have the effect, as explained later, of increasing the activation energy and so would make the calculated reaction rate too low.

BIMOLECULAR REACTIONS

In a surface reaction between two molecules it is presumably necessary that the molecules shall be adsorbed on adjacent sites; the reaction may thus be considered as occurring between one molecule of each of the reactants A and B and a dual site S_2 on the surface of the catalyst: thus

$$A+B+S_2 \rightleftharpoons (A-B-S_2)^{\mp} \rightarrow \text{products.}$$

⁶C. N. Hinshelwood and R. E. Burk, J. Chem. Soc. 127, 1105 (1925).

Soc. 127, 806 (1925). ⁹ Cf. C. N. Hinshelwood and B. Topley, J. Chem. Soc. 123, 1014 (1923).

¹⁰ B. Topley, Nature 128, 115 (1931).

 ⁶C. H. Kunsman, E. S. Lamar and W. E. Deming, Phil. Mag. 10, 1015 (1930).
 ⁷R. E. Burk, Proc. Nat. Acad. Sci. 13, 67 (1927).
 ⁸C. N. Hinshelwood and C. R. Prichard, J. Chem.

It is first required to determine the number of dual sites in terms of the number of available single sites per sq. cm (c_s) and other factors. If the fraction of the surface covered by reactant A is θ , and that covered by B is θ' , then the number of bare sites adjacent to any given site will be $s(1-\theta-\theta')$ where s, as before, is the total number of possible sites adjacent to any given site. The number of dual sites per sq. cm is thus $\frac{1}{2}c_s s(1-\theta-\theta')$, the factor one-half arising from the fact that in the above treatment each dual site is counted twice. The fractions θ and θ' may be expressed in terms of the concentrations of surface adsorbed molecules, or atoms, of A, i.e., c_a , and of B, i.e., $c_{a'}$, as follows,

$$\theta = c_a / (c_a + c_{a'} + c_s) \tag{8}$$

and

$$\theta' = c_{a'}/(c_a + c_{a'} + c_s), \qquad (9)$$

and so the number of dual sites per sq. cm may be written in the form

> Conc. of dual sites $=\frac{1}{2}sc_s^2/L$, (10)

where L stands for $c_a + c_{a'} + c_s$, the total number of sites per sq. cm of bare surface. The theory of absolute reaction rates then gives the velocity of the bimolecular surface reaction as

$$v = \frac{1}{2}s \frac{c_{g}c_{g'}c_{s}^{2}}{L} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_{g}F_{g'}f_{s}} e^{-\epsilon_{0}/kT}, \qquad (11)$$

where c_g and $c_{g'}$ are the concentrations of A and B in the gas phase, and F_q and $F_{q'}$ are their partition functions for unit volume; $f \neq$ and f_s are the partition functions, for the whole surface, of the activated complex and of reaction sites, respectively. Since L is the sum of c_a , $c_{a'}$ and c_s , it is possible to express Eq. (11) in terms of c_g , $c_{a'}$, and c_s by substituting the appropriate values of c_a and $c_{a'}$ given by the adsorption isotherm, Eq. (5). It is convenient, in this connection, to consider a number of special cases.

(a) Sparsely covered surface.-When the surface is sparsely covered, i.e., the sum of c_a and $c_{a'}$ is small, L is practically equal to c_s and hence Eq. (11) becomes

$$v = \frac{1}{2} s c_g c_{g'} c_s \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g F_{g'} f_s} e^{-\epsilon_0/kT}.$$
 (12)

This represents the simplest type of second-order

kinetics, the rate of the heterogeneous reaction being directly proportional to the concentration of each of the reactants: provided c_s is known, e.g., for a smooth sparsely covered surface, it is possible to calculate the reaction rate from Eq. (12).

The velocity of the reaction between nitric oxide and oxygen on a glass surface has been measured¹¹ at 85°K and found to be represented by the expression

$$v = 9.4 \times 10^{-27} c_{\rm NO} c_{O_2} e^{-\epsilon_0/kT}$$
 molecules cm⁻² sec.⁻¹

with concentrations in molecules per cc. In this equation ϵ_0 is the activation energy at 0°K, a slight adjustment having been made, by means of the theoretical Eq. (12), to the experimental activation energy observed at 85°K. The dependence of the rate on the product of the concentrations of the reactants suggests that the activated complex consists of a molecule of NO and one of O₂ adsorbed on neighboring sites on the surface, so that Eq. (12) should be applicable. The ratio of the partition functions for the adsorbed, immobile, activated complex and for the adsorption centers, i.e., $f \pm / f_s$, may be taken as unity, while F_{NO} and F_{O_2} may be calculated in the usual manner for diatomic molecules, the vibrational contributions being very little different from unity at the experimental temperature. Both nitric oxide and oxygen have multiplet ground states and allowance should be made for these in deriving the partition functions, but since the electron multiplicity of the activated complex is unknown it may be assumed that the values cancel each other; this approximation cannot be in error by a factor of more than two or three.¹² Since the experimental results suggest a sparsely covered surface, the number of individual reaction sites, c_s , is about 10¹⁵ per sq. cm. If every site is surrounded by four others, i.e., s is 4, and if two adjacent sites are involved, it is found from Eq. (12) that

$v = 14.8 \times 10^{-27} c_{\rm NO} c_{\rm O_2} e^{-\epsilon_0/k T}$

in good agreement with the experimental result.

(b) One reactant more strongly adsorbed than the other .- If the reactant A is more strongly ad-¹¹ M. Temkin and W. Pyzhow, Acta Physicochimica U. R. S. S. 2, 473 (1935). ¹² Cf. H. Gershinowitz and H. Eyring, J. Am. Chem.

Soc. 57, 985 (1935).

sorbed than B, then $c_{a'}$ may be neglected in comparison with c_a , and L may be put equal to $c_a + c_s$; Eq. (11) then becomes

$$v = \frac{1}{2}s \frac{c_g c_{g'} c_{s'}^2}{c_a + c_s} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g F_{g'} f_s} e^{-\epsilon_g/kT}.$$
 (13)

Writing the adsorption isotherm, as in Part I, in the abbreviated form $c_a/c_s = Ac_a$ where A is equal to $(f_a/F_g f_s)e^{\epsilon/kT}$, and using this relationship to eliminate c_a from Eq. (13), it is found that

$$v = \frac{1}{2} s \frac{c_g c_{g'} c_s}{1 + A c_g} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g F_{g'} f_s} e^{-\epsilon_0/kT}.$$
(14)

Further, since L is approximately equal to $c_a + c_s$, as already seen, it follows (cf. Eq. (46), Part I) that $c_s = L/(1 + Ac_g)$, and substitution for c_s in (14) gives

$$v = \frac{1}{2} s \frac{Lc_g c_{g'}}{(1+Ac_g)^2} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g F_{g'} f_s} e^{-\epsilon_g/kT}, \quad (15)$$

which is equivalent to the more familiar form¹³

$$v = k' p_{\rm A} p_{\rm B} / (1 + B p_{\rm A})^2,$$
 (16)

where k' and B are constants at a definite temperature. It is of interest to note that if $c_{g'}$, or $p_{\rm B}$, is kept constant as c_{g} , or $p_{\rm A}$ is increased, the reaction velocity should pass through a maximum: behavior of this kind has been observed in the reaction between hydrogen and carbon dioxide on platinum.13

(c) One reactant very strongly adsorbed.—If the reactant A is so strongly adsorbed that it occupies most of the available surface, the fraction c_a/c_s , which is equal to Ac_a , is much greater than unity: in Eq. (15) therefore unity may be neglected in comparison with Ac_g , and hence

$$v = \frac{1}{2}s \frac{L}{A^2} \cdot \frac{c_{g'}}{c_y} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g F_{g'} f_s} e^{-\epsilon_0/kT}.$$
 (17)

Expressing A as $(f_a/F_a f_s)e^{\epsilon/kT}$ Eq. (17) becomes

$$v = \frac{1}{2}sL\frac{c_{g'}}{c_g}\cdot\frac{kT}{h}\cdot\frac{F_af_{\pm}f_s}{F_{g'}f_a}e^{-\epsilon_{g'}/kT},$$
 (18)

where ϵ_0' is equal to $\epsilon_0 + 2\epsilon$. The experimental activation energy will thus be greater by 2ϵ than

¹³ C. N. Hinshelwood and C. R. Prichard, J. Chem. Soc. 127, 806 (1925).

the value for a sparsely covered surface of the same material. Equation (18) is equivalent to the expression derived by the method of Langmuir, $v = k' p_{\rm B}/p_{\rm A}$ where $p_{\rm A}$ and $p_{\rm B}$ are the partial pressures of the reactants A and B, which are proportional to c_g and $c_{g'}$, respectively. Several instances of this type of kinetics have been reported.14

Equation (18) may be applied quantitatively to the reaction between carbon monoxide and oxygen on the surface of platinum.¹⁵ At 572°K the observed rate is equal to

$$7.10 \times 10^{14}$$
 molecules cm⁻² sec.

The temperature coefficient corresponds to an activation energy of 33.3 kcal. in this temperature region; the use of this value in Eq. (18) gives a calculated rate of

$$4.33 \times 10^{15}$$
 molecules cm⁻² sec.⁻¹

in satisfactory agreement with experiment. The reaction between hydrogen and oxygen on platinum¹⁵ shows a similar behavior but the data are not sufficiently precise to permit an application of the theory.

BIMOLECULAR REACTION WITH A SINGLE REACTANT

When both reacting molecules are the same, it can be readily seen that the general Eq. (11) simplifies to the form

$$v = \frac{1}{2}s \frac{c_g^2 c_s^2}{L} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g^2 f_s} e^{-\epsilon_0/kT}, \qquad (19)$$

where L is equal to $c_s + c_a$. If the surface is sparsely covered, $L \approx c_s$, and (19) reduces to

$$v = \frac{1}{2} s c_g^2 c_s \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g^2 f_s} e^{-\epsilon_g/kT}, \qquad (20)$$

and the reaction behaves kinetically as a straightforward second-order process. At the other extreme, when the surface is almost completely

¹⁴ For examples, see G.-M. Schwab, Catalysis (Translated New York, 1937), p. 227. ¹⁵ I. Langmuir, Trans. Faraday Soc. **17**, 621 (1922).

covered, L is approximately equal to c_a , and hence $L = A c_g c_s$, and insertion of L/A for $c_g c_s$ in (19) gives

$$v = \frac{1}{2}s \frac{L}{A^2} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_o^2 f_s} e^{-\epsilon_o/kT}.$$
 (21)

The reaction is clearly of zero order, since it is independent of the concentration, or pressure, of the reacting gas. Alternatively, if L is replaced by c_a , then

$$v = \frac{1}{2}s \frac{c_a}{A^2} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_a^2 f_s} e^{-\epsilon_0/kT}.$$
 (22)

In this equation, as in (6), the reaction is treated from the standpoint of the adsorbed molecules; if the value of A, given above, is inserted in Eq. (22), the result is

$$v = \frac{1}{2}sc_a \frac{kT}{h} \cdot \frac{f_{\pm}f_s}{f_a^2} e^{-(\epsilon_0 + 2\epsilon)/kT}, \qquad (23)$$

which may be compared with (6) for a unimolecular reaction. In the present case c_a is also constant, since the surface is almost fully covered, and the velocity of the reaction is independent of the pressure of the reactant, as already recorded. The "surface activation energy" is seen from Eq. (23) to be $\epsilon_0+2\epsilon$.

RETARDATION BY POISONS

Unimolecular reactions.—When the product of a reaction, or other substance, e.g., a poison which may be present in the system, is strongly adsorbed, the process is retarded. For a unimolecular reaction occurring on a single site, the poison also being adsorbed on a single site, the problem is similar to adsorption on a covered surface considered in Part I. An equation exactly analogous to (47) is applicable, except that $f \pm$ is the partition function for the activated state of the reaction and ϵ_1 is the corresponding heat of activation; the rate equation may then be written in the more familiar form

$$v = k' p_{\mathrm{A}} / (1 + B p_{\mathrm{P}}), \qquad (24)$$

where p_P is the partial pressure of the poisoning substance. If the poison is very strongly adsorbed and virtually covers the whole surface, this becomes

$$v = k' p_{\rm A} / p_{\rm P}. \tag{25}$$

For such a surface an equation similar to (48) of Part I is applicable; by utilizing the adsorption isotherms (45) and (45*a*) of Part I, and putting L equal to c_{ap} since the surface is almost completely covered by poison, this equation takes the form

$$v = c_a \frac{kT}{h} \cdot \frac{f_{\pm}}{f_a} e^{-(\epsilon_0 + \epsilon)/kT}, \qquad (26)$$

where ϵ_0 is the heat of activation for the reaction on a clean surface and ϵ is the heat of adsorption of the reactant. This equation again considers the reaction from the standpoint of adsorbed molecules of reactant, and the surface activation energy is seen to be $\epsilon_0 + \epsilon$. The experimental heat of activation, the gas being considered as the reactant, is $\epsilon_0 + \epsilon_p$, where ϵ_p is the heat of adsorption of the product, and if this is represented by ϵ_{exp} . it is seen that the surface activation energy is $\epsilon_{exp} + \epsilon - \epsilon_p$.¹⁶

In Eq. (2) the quantity c_s represents the concentration of reaction centers, irrespective of whether they are single or dual sites; for the present purpose, however, it is necessary to restrict c_s to the concentration of single sites, and then the concentration of dual sites is given by Eq. (10). Inserting this value into Eq. (2), the rate of a unimolecular reaction on dual sites becomes

$$v = \frac{1}{2}s \frac{c_{g}c_{s}^{2}}{L} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_{g}f_{s}} e^{-\epsilon_{g}/kT}.$$
 (27)

If the surface is almost completely covered by a reaction product or other substance acting as a poison, then L can be replaced by c_{ap} , the surface concentration of poison, which may be adsorbed either as molecules or as atoms. Since the latter case is of experimental interest, it alone will be considered; according to Eq. (33) of Part I,

$$c_{ap}/c_s = c_{gp} \frac{f_{ap}}{f_s F_{gp}} e^{\epsilon_p/kT}, \qquad (28)$$

and hence (27) may be written

$$v = \frac{1}{2}sL\frac{c_{\varphi}}{c_{xy}}\cdot\frac{kT}{h}\cdot\frac{F_{\varphi p}f_{\pm}f_{s}}{F_{x}f_{x}^{2}}e^{-(\epsilon_{\varphi}+2\epsilon_{p})/kT} \qquad (29)$$

$$=k'p_{\rm A}/p_{\rm P},\tag{30}$$

¹⁶ Cf. C. N. Hinshelwood, *Kinetics of Chemical Change* (Oxford University Press, 1926, p. 178; 1940, p. 245).

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where c_g and c_{gp} are the concentrations of reactant and poison, respectively, in the gas phase, and p_A and p_P are their partial pressures. The heat of activation is seen to be $\epsilon_0 + 2\epsilon_p$.

The rate of decomposition of ammonia at low pressures on a platinum surface varies as the pressure of the reactant and inversely as that of hydrogen, which acts as a poison;¹⁷ both Eqs. (25) and (30) satisfy these conditions, but the latter is probably applicable, since hydrogen is adsorbed atomically on platinum at high temperatures. It should, therefore, be possible to calculate the rate of reaction by means of Eq. (29). According to the experiments of Schwab and Schmidt the observed rate at 1423°K is $2.60 \times 10^{22} c_{\rm NH_3}/c_{\rm H_2}$ molecules per sq. cm and the energy of activation is 44.3 kcal.¹⁸ Taking this value as equivalent to $\epsilon_0 + 2\epsilon$, and considering f_{\pm} , f_s and f_{ap} to be unity, as usual, the rate of reaction for a smooth surface $(L=10^{15} \text{ per sq. cm},$ s=4) is calculated from Eq. (29) to be $0.92 \times 10^{22} c_{\rm NH_3}/c_{\rm H_2}$ molecules per sq. cm at 1423°K. Equally good agreement is, of course, obtained at other temperatures, since the experimental activation energy is employed in the calculations.

Bimolecular reactions.—If two molecules of a single reactant are involved, Eq. (19) is still applicable, but L is equal to $c_s+c_a+c_{ap}$. If the poison is fairly strongly adsorbed c_a may be neglected in comparison with c_{ap} , and so L will be given by c_s+c_{ap} ; inserting this value in (19), it is seen that

$$v = \frac{1}{2}s \frac{c_g^2 c_s^2}{c_s + c_{ap}} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g^2 f_s} e^{-\epsilon_0/kT}.$$
 (31)

Substituting the value $A_p c_s c_{gp}$ for c_{ap} , Eq. (31) becomes

$$v = \frac{1}{2} s \frac{c_g^2 c_s}{1 + A_p c_{gp}} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g^2 f_s} e^{-\epsilon_0/kT}.$$
 (32)

Utilizing the relationship $c_s = L/(1 + A_p c_{gp})$, i.e.,

Eq. (46) of Part I, it follows that

$$v = \frac{1}{2}s \frac{Lc_o^2}{(1+A_p c_{gp})^2} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_b^2 f_s} e^{-\epsilon_0/kT}$$
(33)

or

$$v = k' \frac{p_{\rm A}^2}{(1 + Bp_{\rm P})^2},$$
 (34)

where p_A and p_P are the pressures of reactant and poison, respectively, the latter being preferentially adsorbed.

If the product is very strongly adsorbed, so that c_s can be neglected in comparison with c_{ap} , L becomes virtually equal to c_{ap} : it is then found that

$$v = \frac{1}{2}s \frac{L}{A_{p^2}} \cdot \frac{c_{g^2}}{c_{gp^2}} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_g^2 f_s} e^{-\epsilon_g/kT}, \qquad (35)$$

where A_p is $(f_{ap}/F_{gp}f_s)e^{\epsilon_p/kT}$. The same result may, of course, be obtained by neglecting unity in comparison with A_pc_{gp} , since A_p will be large for a strongly adsorbed substance, in Eq. (33). The general form of this equation is equivalent to $v=k'p_{\rm A}^2/\dot{p}_{\rm P}^2$ where A denotes the reacting substance, and P the retarding material; the latter retards a bimolecular reaction according to the second power of its pressure, and not to the first, as has frequently been assumed. However, if the retarding gas is composed of diatomic molecules which are adsorbed in the form of atoms the equation takes the form

$$v = \frac{1}{2} s \frac{L}{A_p^2} \cdot \frac{c_g^2}{c_{g,2}} \cdot \frac{kT}{h} \cdot \frac{f_{\pm}}{F_y^2 f_s} e^{-\epsilon_0/kT}, \qquad (36)$$

where A_p has the value $(f_{ap}/F_{ap}{}^{\frac{1}{2}}f_s)e^{\epsilon/kT}$. The reaction rate now varies inversely as the first power of the poison pressure. The quantity A_p^2 , which appears in both Eqs. (35) and (36), involves $e^{2\epsilon_p/kT}$ and so the heat of activation is in each case $\epsilon_0 + 2\epsilon_p$, where ϵ_p is the heat of adsorption of a molecule of poison in the former case and an atom in the latter.

Behavior of the type represented by Eq. (36) has been recorded¹⁹ for the decomposition of nitric oxide on platinum and on a platinumrhodium alloy surface, which is retarded by

¹⁷ G.-M. Schwab and H. Schmidt, Zeits. f. physik. Chemie B3, 337 (1929).

¹⁸ The figure 140 kcal. given by C. N. Hinshelwood and R. E. Burk, J. Chem. Soc. **127**, 1114 (1925) appears to apply at higher pressures when the reaction kinetics are more complicated, as found by G.-M. Schwab and H. Schmidt, reference 14. The high temperature coefficient obtained under these conditions may be due to the operation of a chain reaction [cf. reference 14, p. 316].

¹⁹ P. W. Bachman and G. B. Taylor, J. Phys. Chem. **33**, 447 (1929).

oxygen. At 1483°K on pure platinum the rate is given as

$$v = 2.2 \times 10^{-4} \frac{c_{\rm NO}^2}{c_{\rm O_2}}$$
 molecules cm⁻² sec.⁻¹.

Since the oxygen is adsorbed atomically on platinum Eq. (36) should be applicable. Assuming f_{\pm} , f_s and f_{ap} to be unity, and taking the activation energy to be 14 kcal.,²⁰ the calculated rate is found to be

$$v = 2.9 \times 10^{-4} \frac{c_{\rm NO}^2}{c_{\rm O_2}}$$
 molecules cm⁻² sec.⁻¹,

in excellent agreement with experiment.

Similar equations may be deduced for the cases in which the two reacting molecules are different: these are analogous to (33) and (34), except that $c_g c_{g'}$ replaces $c_{g'}^2$, where c_g and $c_{g'}$ are the concentrations of the two reacting gases, and $F_g F_{g'}$ is used instead of F_g^2 . No cases appear to be known in which equations of the resulting type are applicable, but the reaction between sulfur dioxide and oxygen on platinum is the nearest approach. The product, i.e., sulfur trioxide, undoubtedly retards the reaction, but the reaction rate is not inversely proportional to the square of its pressure as the theoretical treatment predicts.

DISSOCIATION OF HYDROGEN ON TUNGSTEN

When a tungsten filament is heated in an atmosphere of hydrogen, the latter is converted into the atomic form which evaporates off from the surface of the tungsten and is generally adsorbed by the glass walls of the reaction vessel.²¹ The rate of formation of atomic hydrogen has been found,²² over a range of temperature (1148° to 1420°K) and pressure (3×10^{-3} to 3.7×10^{-2} mm of mercury) to be proportional to the square-root of the pressure. This result indicates clearly that the activated complex of the reaction consists of hydrogen atoms, and not molecules (cf. Part I), and hence the rate equation should be

$$v = c_{\rm H_2}{}^{\frac{1}{2}}c_s \frac{kT}{h} \cdot \frac{f_{\pm}}{F_{\rm H_2}{}^{\frac{1}{2}}f_s} e^{-\epsilon_0/kT}.$$
 (37)

The partition functions of the activated state and of the reaction centers on the surface may both be taken as unity, for even if the former consisted of a free hydrogen atom it would be hemmed in by its neighbors and so have no freedom of movement. Equation (37) may thus be written in the form

$$v = c_{\mathrm{H_2}} \frac{kT}{k} \cdot \frac{1}{\frac{(2\pi mkT)^2}{h^2}} \left(\frac{8\pi IkT}{2h^2}\right)^2} e^{-E_0/RT}.$$
 (38)

The mechanism of the formation of atomic hydrogen on a tungsten surface appears to be the adsorption of a molecule, then an atom jumps to another site, becomes detached from the surface-this constitutes the activated state-and finally escapes into the gas phase. Since the initial state in the reaction is $\frac{1}{2}H_2$ and the final state is H, the process is endothermic to the extent of one-half the heat of dissociation of molecular hydrogen, i.e., 51.5 kcal. at 0°K. The activation energy of the process under consideration should thus have at least this value, and if E_0 is assumed to be 51.5 kcal. it is possible to calculate the rate of the reaction, at various temperatures, by means of Eq. (38); the surface is assumed to be sparsely covered, so that c_s may be taken as 10¹⁵ per sq. cm. The results, expressed as atoms cm⁻² sec.⁻¹, are compared with the experimental rates²¹ in Table III, the pressure being in mm of mercury. It is of interest to call attention to the fact that in this particular reaction the simple assumption that the activated state consists of hydrogen atoms permits the absolute rate of dissociation of hydrogen on a tungsten surface to be calculated with an accuracy which is probably as good as that attained by experiment.

According to the observations of R. C. L. Bosworth²³ the surface is almost fully covered

TABLE III.

	RATE OF DISSOCIATION			
Темр.	Obs.	CALC.		
1148°K	6.6×10 ¹⁵ √⊅	3.3×1015√¢		
1243	3.0×10^{16}	1.8×10^{16}		
1378	1.1×10^{17}	8.0×10^{16}		
1420	2.9×10^{17}	2.4×10^{17}		

²³ R. C. L. Bosworth, Proc. Camb. Phil. Soc. 33, 394 (1937).

²⁰ G. E. Green and C. N. Hinshelwood, J. Chem. Soc. 1709 (1936).

²¹ I. Langmuir, J. Am. Chem. Soc. **34**, 1310 (1912); **37**, 417 (1915). ²² G. Bryce, Proc. Camb. Phil. Soc. **32**, 648 (1936).



with hydrogen under the conditions employed in obtaining the data in Table III. Since the formation of atomic hydrogen is not of zero order, it is apparent that even if the surface as a whole were largely covered, the active centers on which reaction occurs can be only sparsely covered. If the experiments on the extent of coverage of the surface are correct, therefore, the active centers must constitute a fraction only of the total number of tungsten atoms on the surface. In view of the agreement between observed and calculated rates in Table III, the latter being based on the assumption of a bare surface, this fraction must be relatively large.

Comparison of Homogeneous and Heterogeneous Reactions

The reaction rate per sq. cm of surface for a second-order heterogeneous reaction may be written (cf. Eq. (12)) as

$$v_{\rm het.} = c_{\rm A} c_{\rm B} c_s \frac{kT}{h} \cdot \frac{1}{F_{\rm A} F_{\rm B}} e^{-E_{\rm het.}/RT}, \qquad (39)$$

where the reactants are designated by A and B; the partition functions of the activated complex and of the reaction centers have been taken as unity. For the corresponding process occurring entirely in the gas phase, the rate equation, according to the theory of absolute reaction rates, is given by

$$v_{\text{hom.}} = c_A c_B \frac{kT}{h} \cdot \frac{F_{\pm}}{F_A F_B} e^{-E_{\text{hom.}}/RT}.$$
(40)

It follows, therefore, that

$$\frac{v_{\text{het.}}}{v_{\text{hom.}}} = \frac{c_s}{F_{\pm}} e^{\Delta E/RT}, \qquad (41)$$

where ΔE is equal to $E_{\rm hom.} - E_{\rm het.}$, i.e., the amount that the activation energy of the homogeneous reaction is greater than that of the heterogeneous process. For one sq. cm of smooth surface, c_s is about 10¹⁵ whereas the partition function F_{\pm} for the activated complex of the homogeneous gas reaction is at least 10²⁴ (for hydrogen) and is often of the order of 10³⁰ per cc; taking 10²⁷ as a mean value for F_{\pm} , it follows that

$$v_{\rm het.}/v_{\rm hom.} \approx 10^{-12} e^{\Delta E/RT},$$
 (42)

the heterogeneous rate being that for one sq. cm of surface, and the homogeneous rate for one cc of the gaseous reactants. It is obvious, therefore, that if a heterogeneous reaction is to be as fast as a homogeneous one involving the same reactants at the same pressures, either a very large surface, viz., 1012 sq. cm, must be employed, or alternatively the activation energy for the heterogeneous reaction must be considerably less than that for the homogeneous process. At a temperature of 500°K, for example, the reaction per sq. cm of surface will have the same rate as the gas reaction per cc, only if the activation energy of the former is about 27.6 kcal. less than that of the latter. At lower temperatures the difference would need to be smaller, e.g., 16.5 kcal. at 300°K.

It may appear surprising, at first sight, in view of the much smaller activation energy necessary for a heterogeneous reaction to have the same rate as the corresponding homogeneous one, that catalyzed reactions are frequently so much faster than those which take place entirely in the gas phase. The reason is twofold: in the first place the surface area of the catalyst is very large, so that the reaction is not restricted to one sq. cm as has been assumed in the above calculations; and in the second place, the activation energy for a heterogeneous reaction is generally less than for the same process in the gas phase.²⁴

It is of interest to inquire next into the circum-

²⁴ Cf. C. N. Hinshelwood, reference 16 (1940), p. 224.

stances which make it possible for the activation energy of the heterogeneous reaction to be less than for that occurring wholly in the gas phase: this may be most easily seen with the aid of a potential energy diagram. The full line in Fig. 1 represents the variation of potential energy in the decomposition coordinate for the homogeneous reaction, while the dotted curve represents the change during the course of the heterogeneous reaction. It will be seen that the surface reaction involves first the adsorption of the reactants. then the formation of an adsorbed activated complex which decomposes to give adsorbed resultants, and finally the latter must be desorbed. The difference between $E_{\text{hom.}}$ and $E_{\text{het.}}$ is seen to be equal to the difference in potential energy between the activated state in the gas phase and on the surface, and hence is equal to the heat of adsorption of the activated complex. If the reactants undergo activated adsorption, it is very probable that the activated complex for the reaction on the surface will consist virtually of atoms or free radicals, and these are likely to have a high energy of adsorption. Under these circumstances $E_{het.}$ is likely to be very much lower than $E_{\text{hom.}}$. The decrease in the activation energy for the hydrogen-oxygen reaction and the decompositions of hydrogen iodide and methane on surfaces, as compared with the same homogeneous reactions, has been explained²⁵ somewhat in this manner.

If all the active centers of the surface are covered by one of the products of the reaction or by some other material which is strongly adsorbed and so acts as a poison, then since these must be desorbed before an activated complex can be formed on the surface, the heat of activation is increased by an amount equal to the heat of adsorption of the poison, as seen above. There is some compensation for this increase, however, by the increase of entropy accompanying the desorption of the poison, and the situation is very similar to that considered in Part I in connection with the rate of adsorption on a poisoned surface. As in that instance, the free energy of activation for reaction on such a surface is greater than the value for an unpoisoned surface by an amount equal to the standard free energy of desorption of the poison. It will be noted that in all poisoned reactions, a function of the concentration (or pressure) of the poison in the gas phase appears in the denominator of the rate equation, so that the greater the pressure of the retarding gas the slower the reaction rate.

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²⁵ M. Polanyi, Zeits. f. Elektrochemie **27**, 143 (1921); G.-M. Schwab and E. Pietsch, *ibid.*, **32**, 430 (1926); Zeits. f. physik. Chemie **121**, 189 (1926); **126**, 473 (1927); H. S. Taylor, J. Phys. Chem. **30**, 145 (1926).