[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Adsorption Kinetics. I. The System of Alkali Atoms on Tungsten[1]

BY IZUMI HIGUCHI, TAIKYUE REE AND HENRY EYRING

RECEIVED MAY 16, 1955

All the alkali atoms adsorbed on a tungsten surface are assumed to be adsorbed in an ionic state forming an electric double layer at the surface. The so-called "contact potential," V, which is the potential difference between this layer and the surface, is given by the Helmholtz equation. Because of the field of the double layer, the desorption (adsorption) heat, the activation heat and the activation free energy for the desorption decrease with surface coverage, θ. The decrease of these quantities, $\delta(\Delta H)$, $\delta(\Delta H^\ddagger)$ and $\delta(\Delta F^\ddagger)$, respectively, are theoretically given as a function of V, which is in turn a function of θ. The Becker–Zeldovich equation for the rate of desorption, $-\,\mathrm{d}\theta/\mathrm{d}t = a\theta \exp(b\theta)$, is derived from the theory of rate processes. The physical meaning of the constants a and b are as follows: a is the frequency with which an adion on a bare surface transforms to an adatom. b indicates the ratio of the decrease of the activation free energy for the desorption, $\delta(\Delta F_1^\ddagger)$, at $\theta = 1$ to the mean kinetic energy of the adion, RT. In order to test the authors' theory, the parameters d_0 (the distance of the adsorbed layer from the surface) and α (the polarizability of the adion) were determined from the experimental values of V. The values of these parameters are reasonable compared to the radii and the polarizabilities of the adions. Using these parameters, the values of $\delta(\Delta H)$ (which equals $\delta(\Delta H^\ddagger)$ in the present case), $\delta(\Delta F^\ddagger)$, and b were calculated. The agreement between theory and experiment is satisfactory. Our theory has been applied to the systems Cs on W, K on W, Na on W and Ba on W.

Introduction

Chemisorption, or activated adsorption, is a fundamental process in heterogeneous catalysis. The kinetics of chemisorption, however, has not been studied well compared with catalysis itself. Frequent attempts have been made to represent the course of chemisorption by a formula. Most of the formulas are empirical, and limited to one particular substance.

In 1929 Becker[2] found that the equation

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = a\theta e^{b\theta} \qquad (1)$$

describes correctly the rates of desorption of cesium atoms and ions on a tungsten surface. In equation 1, θ is the fraction of the surface covered by the adsorbate, a and b are constants. As far as we know, this is the first use of an exponential function of θ in adsorption kinetics. In 1934 Zeldovich,[3] and Roginski and Zeldovich[4] expressed the rate of adsorption of carbon monoxide on finely divided manganese dioxide between −78 and −39° by the equation

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = a(1 - \theta)e^{-b\theta} \qquad (2)$$

The general applicability of equation 2 was shown by Roginski[5] in 1934. He applied this equation to the rates of adsorption of nitrogen on iron, oxygen on silver, hydrogen on zinc oxide and ethylene on nickel. Elovich and Roginski[6] applied equation 2 to the catalytic oxidation of carbon monoxide on manganese dioxide (1937). In 1939 Elovich and Zhabrova[7] found that equation 2 is applicable for the rates of adsorption of hydrogen and ethylene on reduced nickel between −23 and +50°, and also to the rate of hydrogenation of ethylene on the same catalyst. The broad applicability of equation 2 was shown by Taylor and Thon[8] for a wide variety of cases studied by many authors. Porter and Tomkins[9] applied equation 2 to the chemisorption of hydrogen, carbon monoxide and nitrogen on evaporated iron films with good results.

As mentioned above, equation 1 is for the rate of *desorption*, while equation 2 is for the rate of *adsorption*. The form of these two equations are essentially the same except for the positive and negative signs in the exponent which are, as our theory shows, due to the fact that adsorption is a reverse process of desorption, and *vice versa*. We refer to (1) or (2) as the Becker–Zeldovich equation.[10]

Since the paper of Taylor and Thon[8] came out, several theoretical efforts have been made to explain the Becker–Zeldovich equation.[8,11,13,14] The merits of these theories are discussed in two review articles.[11b,12] We first consider the desorption of alkali atoms from a tungsten surface, since this is one of the simplest cases. We derive the Becker–Zeldovich equation from the absolute reaction rate theory, assuming the adsorption layer is a Helmholtz double layer. The physical significance of the constants a and b will thus be clarified.

The Structure of the Adsorbed Layer.—It is a well-known fact that alkali atoms are adsorbed as an ionic layer on a tungsten surface as shown in Fig. 1. The negative charges in Fig. 1 are the electric images of the positive ions. The potential difference between the adsorbed layer and the metal surface, which is called the contact potential,

---

[1] Presented in the division of physical and inorganic chemistry of the 127th national American Chemical Society meeting at Cincinnati, Ohio, April 4, 1955.

[2] J. Becker, *Trans. Am. Electrochem. Soc.*, **55**, 153 (1929).

[3] Ya. Zeldovich, *Acta Physicochim. U.S.R.R.*, 1, 449 (1934).

[4] S. Roginski and Ya. Zeldovich, *ibid.*, **1**, 554, 595 (1934).

[5] S. Roginski, *Nature*, **134**, 935 (1934).

[6] S. Y. Elovich and S. Roginski, *Acta Physicochem. U.S.S.R.* 1, 295 (1937).

[7] S. Y. Elovich and G. M. Zhabrova, *Zhur. fiz. Khim.*, **13**, 1716, 1775 (1939).

[8] H. A. Taylor and N. Thon, THIS JOURNAL, **74**, 4169 (1952); *ibid.*, **75**, 2747 (1953).

[9] A. S. Porter and F. C. Tomkins, *Proc. Roy. Soc.* (*London*), **A217**, 529, 544 (1953).

[10] In several papers recently published,[8,11,12] equation 2 is referred to as the Elovich equation. Roginski,[5] however, has given Zeldovich credit for equation 2; this is in accord with the chronological order of publication. ADDED ON THE PROOF.—Also P. T. Landsberg (*J. Chem. Phys.*, **23**, 1079 (1955)) has claimed that it is a misnomer to call equations 1 and 2 Elovich's equation.

[11] (a) J. E. German, *Compt. rend.*, **238**, 236, 345 (1954); (b) C. Kemball, "Annual Review of Physical Chemistry," Vol. 4, Annual Reviews Inc., Stanford, California, 1953, p. 309.

[12] K. J. Laidler, Emmett's "Catalysis," Vol. 1, Reinhold Publ. Corp., New York, N. Y., 1954, pp. 189–191.

[13] (a) M. A. Cook and A. G. Oblad, *Ind. Eng. Chem.*, **45**, 1456 (1953); (b) D. D. Eley, *Trans. Faraday Soc.*, **49**, 643 (1953).

[14] H. J. Engell and K. Hauffe, *Z. Elektrochem.*, **57**, 762, 773, 776 (1953).

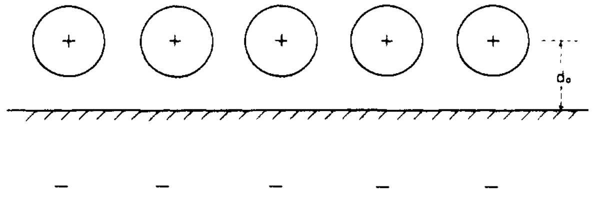

Fig. 1.—The electric double layer formed by adsorbed ions. The negative charges are the images of the positive charges.

V, is given by Helmholtz's equation

$$V = \frac{4\pi\sigma_m\theta e d_0}{\epsilon} \qquad (3)$$

Here, σ_m is the number of adsorption sites per unit area, e is the electronic charge ($e = 4.80 \times 10^{-10}$ e.s.u.), d_0 the distance between the ion and the metal surface, and ϵ is the dielectric constant of the adsorbed layer. The field intensity E and electric displacement D are given as

$$E = \frac{c\mu\theta}{\epsilon} = \frac{D}{\epsilon} \qquad (4)$$

where the relations

$$\left.\begin{array}{ll} \text{(a)} & E = V/d_0 \\ \text{(b)} & \mu = ed_0 \\ \text{(c)} & c = 4\pi\sigma_m/d_0 \end{array}\right\} \qquad (5)$$

are introduced into (3). The dielectric constant ϵ for such a system is not known, but is of the form

$$\epsilon = 1 + c\alpha\theta \qquad (6a)$$

where α is the polarizability of the adsorbed ion.

Equation 6a is derived from the fundamental equations in electrodynamics

$$D = E + 4\pi P \qquad (6b)$$

$$P = n\alpha F \qquad (6c)$$

under the assumption that the adsorbed alkali ions are polarized in the field E. Here, P is the polarization of the medium (*i.e.*, alkali ions), F, the actual field acting on the ion, n, the number of the alkali ions per unit volume. If F equals E, as it does actually, the substitution of equation 6c into (6b) yields equation 6a, because $\epsilon = D/E$ and $n = \sigma_m\theta/d_0$.

The quantity ϵ given by (6a) is a dielectric constant in the normal direction of the double layer, E being the field in the normal direction. We assume

$$E_{\textcircled{H}} = E\cos\textcircled{H} \qquad (6d)$$

where $E_{\textcircled{H}}$ is the field in the direction of angle $\textcircled{H}$ from the normal. Equation 6d is a reasonable assumption, since $E_{\textcircled{H}} = E$ and $E_{\textcircled{H}} = 0$ when $\textcircled{H} = 0$ and $\textcircled{H} = \pi/2$, respectively. These boundary conditions are actually true. From equations 6b, 6c and 6d, and with the assumption $E = F$, we obtain

$$\epsilon_{\textcircled{H}} = \epsilon/\cos\textcircled{H} \qquad (6e)$$

where $\epsilon_{\textcircled{H}}$ ($= D/E_{\textcircled{H}}$) is the dielectric constant in the direction of $\textcircled{H}$. Thus, $\epsilon_{\textcircled{H}} = \epsilon$ and $\epsilon_{\textcircled{H}} = \infty$ when $\textcircled{H} = 0$ and $\pi/2$, respectively. Equation 6e will be used later.

Substituting equation 6a into (3) and (4), one obtains

$$V = \frac{4\pi\sigma_m\theta\mu}{1 + c\alpha\theta} = \frac{V_0\theta}{1 + c\alpha\theta} \qquad (7)$$

$$E = \frac{c\mu\theta}{1 + c\alpha\theta} \qquad (8)$$

where

$$V_0 = 4\pi\sigma_m e d_0 \qquad (9)$$

Equation 7 and 8 are identical in form with the Miller equations.[15] However, it is here derived in quite a different way.

Potential Profile.—The profile of the potential surface for desorption is as shown in Fig. 2. Here, curve I is the curve for the atom adsorbed in an ionic state, and curve II is for the atom adsorbed by van der Waals forces. Thus, the desorption occurs when an ion in the state of curve I changes to curve II. The activation heat, $\Delta H_0{}^\ddagger$, for the desorption and the desorption heat, ΔH_0, when $\theta = 0$ are approximately equal in Fig. 2. This equality is justified by the experimental fact that the adsorption process does not need any activation heat. It is also experimentally true that the activation heat for the desorption, $\Delta H^\ddagger$ at coverage θ, decreases with increasing θ as shown in Fig. 2. Conversely, the activation heat for the adsorption, $\Delta H_a{}^\ddagger$, increases with increasing θ. In the system alkali atom on tungsten, however, the increase is very small considering that the adsorption rates are invariably fast even with high value of θ. We may assume, therefore, that $\Delta H^\ddagger$ is approximately equal to ΔH, the desorption heat at coverage θ (*cf.* Fig. 2). Thus, we have

$$\delta(\Delta H^\ddagger) \simeq \delta(\Delta H) \qquad (10)$$

$$\delta(\Delta H^\ddagger) = \Delta H_0{}^\ddagger - \Delta H^\ddagger \qquad (10a)$$

where

$$\delta(\Delta H) = \Delta H_0 - \Delta H \qquad (10b)$$

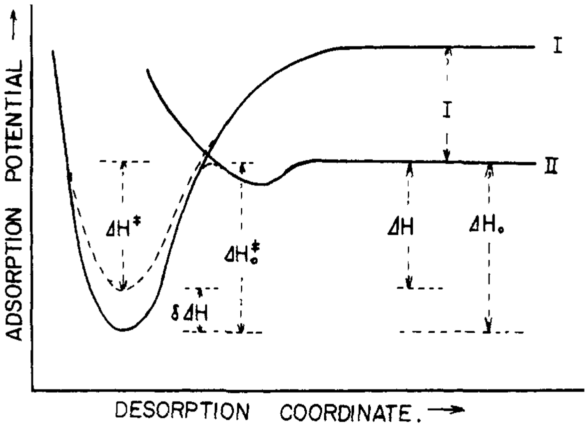

Fig. 2.—Potential curves for the adsorption of alkali atoms on tungsten. Curve I is for ionic adsorption and curve II for atomic adsorption. The broken potential curve indicates the potential shift due to the field of the electric double layer.

The decrease of the activation heat for desorption and of the desorption heat, *i.e.*, $\delta(\Delta H^\ddagger)$ and $\delta(\Delta H)$, is due to the effect of the double layer. Because of the electric field of the double layer, the stability of the adsorbed ions is decreased. The detailed consideration will be given shortly.

Rate Theory of the Desorption.—The rate of the desorption is theoretically given by the equation

$$-\frac{d\theta}{dt} = \theta k' e^{\frac{\delta(\Delta F^\ddagger)}{RT}} - (1 - \theta)pk_a' e^{-\frac{\delta(\Delta F_a{}^\ddagger)}{RT}} \qquad (11a)$$

Here, $\delta(\Delta F^\ddagger)$ is the decrease of activation free energy for the desorption (*i.e.*, $\delta(\Delta F^\ddagger) = \Delta F_0{}^\ddagger - \Delta F^\ddagger$),

---

[15] A. R. Miller, *Proc. Camb. Phil. Soc.*, **42**, 292 (1946); "The Adsorption of Gases on Solids," Cambridge University Press, Cambridge, England, 1949, p. 107.

$\delta(\Delta F_a^{\ddagger})$ is the increase of the activation free energy for adsorption (*i.e.*, $\delta(\Delta F_a^{\ddagger}) = \Delta F_a^{\ddagger} - \Delta F_a^{\ddagger}{}_{(0)}$); k' and k'_a are the rate constants at zero coverage for desorption and adsorption, respectively. The quantities, k' and k'_a are given as

$$k' = \kappa \frac{kT}{h} e^{-\frac{\Delta F_0^{\ddagger}}{RT}} \tag{11b}$$

$$k_a' = \kappa \frac{kT}{h} e^{-\frac{\Delta F_a^{\ddagger}{}_{(0)}}{RT}} \tag{11c}$$

The second term on the right of equation 11a is due to the readsorption of the desorbed atoms. In the measurements of the desorption rates, the experimental conditions are so arranged that readsorption is prevented. Equation 11a, therefore, is written as

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = \theta k' e^{\frac{\delta(\Delta F^{\ddagger})}{RT}} \tag{12}$$

Comparing equation 12 with 1, one finds the relations

$$a = k' \tag{13}$$

$$b = \frac{\delta(\Delta F^{\ddagger})}{\theta RT} = \frac{\delta(\Delta F_1^{\ddagger})}{RT} \tag{14a}$$

The second equality is based on the fact

$$\delta(\Delta F^{\ddagger}) = \delta(\Delta F_1^{\ddagger})\theta \tag{14b}$$

where $\delta(\Delta F_1^{\ddagger})$ is a constant, and is equal to the decrease of the activation free energy at coverage $\theta = 1$. Equation 14b is a necessary and sufficient condition that the second term in equation 14a be independent of θ. Substitution of (14b) into (12) yields

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = \theta k' e^{\frac{\delta(\Delta F_1^{\ddagger})}{RT}\theta} \tag{14c}$$

Thus, the physical meaning of the constants a and b, in the Becker–Zeldovich equation for this model have been clarified. That is, the constant a represents the frequency with which an ion adsorbed on a bare surface changes to an atom. The constant b indicates the ratio of the decrease of the activation free energy for the desorption at $\theta = 1$ to the mean kinetic energy of the adsorbed ions.

From thermodynamic considerations, we have

$$\begin{aligned}\delta(\Delta F^{\ddagger}) &= \delta(\Delta H^{\ddagger}) - T\delta(\Delta S^{\ddagger}) \\ &= \delta(\Delta H) - T\delta(\Delta S^{\ddagger})\end{aligned} \tag{15}$$

where $\delta(\Delta S^{\ddagger}) = \Delta S_0^{\ddagger} - \Delta S^{\ddagger}$. In the second equality in (15), the relation (10) was introduced.

Calculations of $\delta(\Delta H)$.—In order to give quantitative support to our theory, we calculate $\delta(\Delta H)$, the decrease of the desorption heat with increasing coverage, θ. The quantity $\delta(\Delta H)$ is related to the quantity $\delta(\Delta F^{\ddagger})$ by equation 15, while $\delta(\Delta F^{\ddagger})$ is related to the constant b in turn by equation (14a).

For the desorption heat, ΔH_0, from a surface which is nearly bare, the following equation is given[16]

$$\Delta H_0 = e\varphi - I + \frac{e^2}{4d_0} \tag{16}$$

where φ is the work function for tungsten, I is the ionization energy for an alkali atom, and $e^2/(4d_0)$ is the interaction energy between an ion and its electrical image.

We have assumed in Section I that the adsorbed layer is a kind of parallel plate capacitor. The field energy of the latter, $\bar{U}_f$, per unit area is

$$\bar{U}_f = \frac{\epsilon E^2}{8\pi} d_0 = \frac{D^2 d_0}{8\pi\epsilon} \tag{17}$$

the volume of a column between unit areas on the two plates being d_0. The field having the energy $\bar{U}_f$ is created by the adsorption of $\sigma_m\theta$ ions. The field energy, U_f, created by one ion adsorbed on the surface with coverage θ is, therefore, given from equation 17 as

$$U_f = \frac{\partial \bar{U}_f}{\partial(\sigma_m\theta)} = \frac{d_0}{8\pi\sigma_m}\left(2D\frac{\partial D}{\partial\theta} - \frac{D^2}{\epsilon^2}\frac{\partial\epsilon}{\partial\theta}\right) \tag{18}$$

The substitutions of D and ϵ from equation 4 and 6a, respectively, into (18) yield

$$U_f = \frac{c\mu^2\theta}{1 + c\alpha\theta} - \frac{c\mu^2\theta \times c\alpha\theta}{2(1 + c\alpha\theta)^2} \tag{19}$$

Here equation 5c has also been used. That is, an ion adsorbed on the surface with coverage θ liberates the energy U_f when it desorbs from the surface.

Ions adsorbed on a surface with partial coverage of ions experience other attractive forces besides the image force. These attractive forces are due to the interactions between the representative ion and the image charges of its neighboring adsorbed ions. The energy U_i due to the attractive forces is calculated as follows: let A in Fig. 3 be the representative ion. As a first approximation, the image charges are assumed to be uniformly distributed on the $x \sim y$ plane. Take a surface element dS in the form of a ring on the $x \sim y$ plane (*cf.* Fig. 3). The potential energy dU_i of the ion due to the image charges on the surface element dS, is

$$\mathrm{d}U_i = -\frac{\nu\sigma_m\theta e^2 \mathrm{d}S \cos \Theta}{(1 + c\alpha\theta)\mathrm{r}} \tag{20}$$

where r is the distance between the representative ion and the surface element, dS; and Θ is the angle between the z-axis and the radius vector, $\vec{\mathrm{r}}$. In the derivation of (20) use is made of (6e). The factor ν comes from the following fact. The representative ion experiences, also, repulsive forces due to the interactions between it and its neighboring positive

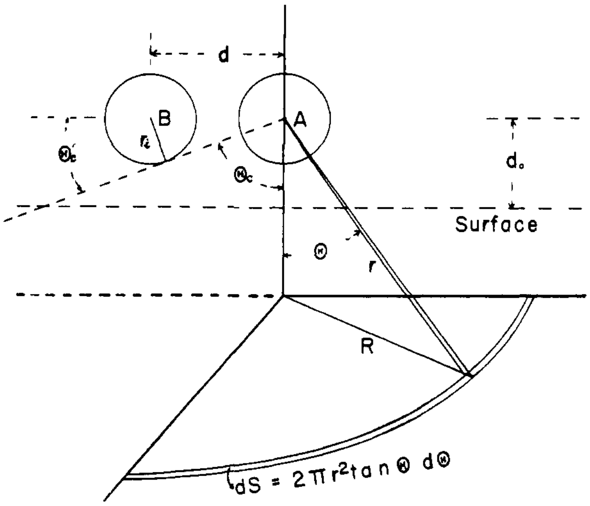

Fig. 3.—Interaction between an adion and image charges.

---

[16] J. H. de Boer, "Electron Emission and Adsorption Phenomena," The Macmillan Co., New York, N. Y., 1935, p. 81.

ions. As long as the ion lies on the same plane with its positive neighbors, the interactions are zero, since they have on this plane only horizontal components which are symmetrical with respect to the ion. If the ion is displaced from the plane even a short distance, however, it experiences strong repulsive forces from the positive neighbors. These repulsive forces cut the interaction energy, U_i, as though the charge of the representative ion were νe $(0 < \nu < 1)$. To make it fit the experiment, we use $^1/_4$ for ν. The surface element dS is represented by (*cf.* Fig. 3)

$$\mathrm{d}S = 2\pi r^2 \tan \Theta \, \mathrm{d}\Theta \qquad (21)$$

The substitution of equation 21 into 20 and the integration of the latter yields

$$U_i = \frac{c\mu^2\theta}{1 + c\alpha\theta}\,\frac{C}{4} \qquad (22)$$

where

$$C = \ln (\cos \Theta_c) \qquad (23)$$

The quantity Θ_c, in equation 23, is the upper limit of the integration, zero being the lower limit. The upper limit, Θ_c, is the angle at which the shielding by neighbors of the image forces is complete. In Fig. 3, the letter B represents a neighboring ion of the representative ion, A, adsorbed at a distance d from the latter. From Fig. 3, one obtains

$$\cos \Theta_c = \sin \Theta_c' = r_i/d \qquad (24)$$

where r_i is the radius of the adsorbed ion, Θ_c' is the complement of Θ_c. The distance, d, is related to the coverage, θ, by the equation

$$d = d_1/\sqrt{\theta} \qquad (25)$$

Here d_1 is the distance between two neighboring ions when $\theta = 1$. From equations 22, 23, 24 and 25 one obtains

$$U_i = -\frac{c\mu^2\theta}{1 + c\alpha\theta} \times \frac{1}{4} \ln \left(\frac{d_1}{r_i\sqrt{\theta}}\right) \qquad (26)$$

Thus, the following results from equation 19 and 26

$$\delta(\Delta H) = U_f + U_i$$
$$= \frac{c\mu^2\theta}{1 + c\alpha\theta}\left(1 - \frac{c\alpha\theta}{2(1 + c\alpha\theta)} - \frac{1}{4}\ln\frac{d_1}{r_i\sqrt{\theta}}\right) \qquad (27)$$

Calculations of $\delta(\Delta F\ddagger)$.—Experimentally, it is known that the decrease of activation free energy, $\delta(\Delta F^{\ddagger})$, for desorption is a linearly increasing function of θ, and that it is equal to $\delta(\Delta H)$ when θ is very small. Thus, we assume that $\delta(\Delta F^{\ddagger})$ is given in the whole range of θ by the formula

$$\delta(\Delta F\ddagger) = c\mu^2\theta\left(1 - \frac{1}{4}\ln\frac{d_1}{r_i\sqrt{\theta_m}}\right) \qquad (28)$$

Equation 28 is obtained by introducing into (27) the condition that when $\theta = \theta_m$, $1 >> c\alpha\theta$. Thus, $\delta(\Delta F^{\ddagger})$ is a linear function of θ in accord with experiment. Introducing equation 28 into 14a, we obtain

$$b = \frac{c\mu^2}{RT}\left(1 - \frac{1}{4}\ln\frac{d_1}{r_i\sqrt{\theta_m}}\right) \qquad (29)$$

Thus, we can calculate the constant b from equation 29, and compare it with the experimental values of b.

The Tests of the Theory. A. Contact Potentials Varying with Surface Coverage.—The curves of contact potentials, V, of metals *versus* the surface coverage, θ, with adsorbates have been determined by many investigators. From these curves, we can determine the parameters which are needed for the tests of our theory. That is, applying equation 7 to the curves of V *versus* θ for the systems Cs on W,[17a] K on W,[18a] Na on W,[18a] and Ba on W,[19] the parameters V_0 and $c\alpha$ are evaluated, and are listed in Table I. Using the parameters, the values of V are recalculated as a function of θ from equation 7. The results are shown in Fig. 4.[20] The good agree-

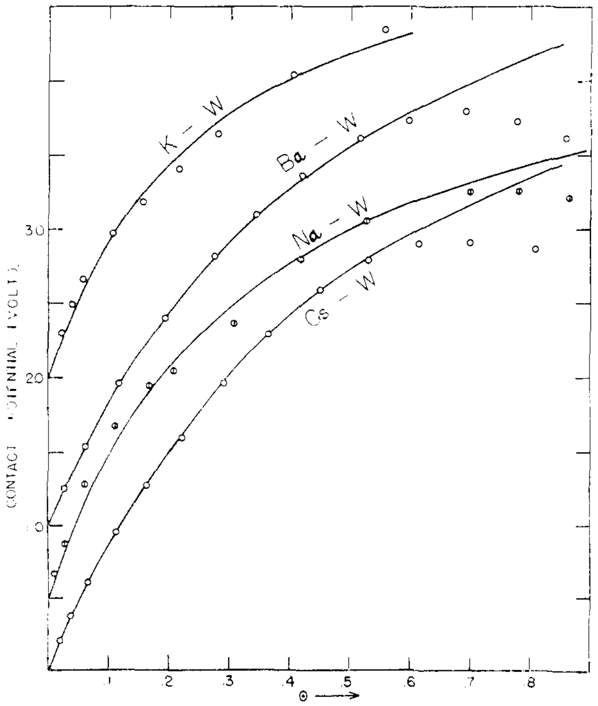

Fig. 4.—Contact potential as a function of surface coverage, θ. The curves for Na–W, Ba–W and K–W systems are shifted upward by 0.50, 1.00 and 2.00 volts, respectively. The full curves represent the values calculated from equation 7. The experimental data for Cs–W are taken from reference (17a); for K–W and Na–W, from (18a); for Ba–W, from (19).

---

(17) (a) J. B. Taylor and I. Langmuir, *Phys. Rev.*, **44**, 423 (1933); (b) I. Langmuir, THIS JOURNAL **54**, 2798 (1932).

(18) (a) R. C. L. Bosworth and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A162**, 1 (1937); R. C. L. Bosworth, *J. Proc. Roy. Soc. N. S. Wales*, **79**, 53 (1945); (b) *Proc. Roy. Soc.*, **A162**, 32 (1937).

(19) J. A. Becker, *Phys. Rev.*, **34**, 1323 (1929).

(20) In Fig. 4, the experimental data for the systems Cs on W and Na on W are obtained from references (17) and (18), respectively. The data for the system K on W are calculated from the "effective dipole moments" given in reference (18). The data for the system Ba on W are due to Becker (19). This author did not measure directly the value of σ, the number of adsorbed barium ions, but calculated σ from the time of exposure, t, during which a tungsten surface is exposed to barium vapor. In the calculation, Becker assumed the maximum in the diagram of V *versus* exposure time was at the point for which $\theta = 1$. Other σ values were calculated from the relation, $\sigma = \sigma_m t/t_m$, where σ_m and t_m are the respective values of σ and t at the maximum. Becker calculated σ_m using the radius of Ba$^+$ (1.53 Å.), and further assuming a close packing of the ions on a plane surface of tungsten. Because of these assumptions, these calculated values of σ_m and σ are large compared to other systems. We recalculated Becker's data, taking $\sigma_m = 3.56 \times 10^{14}$/cm.^{2} and $\theta_{max.} = 0.67$ in agreement with Taylor and Langmuir.[17] Thus, the θ values in Fig. 4 for the system of Ba on tungsten are obtained by multiplying 0.67 into the original θ values of Becker.

ment between the calculated and experimental values indicates the validity of Miller's formula—our equation 7. Boudart[21] has shown the applicability of Miller's formula to the system of cesium on tungsten.

Having the values of V_0 known, it is possible to calculate d_0, the distance from the adsorbed ion to the tungsten surface, from equation 9. The values of d_0 thus obtained are tabulated in the fifth column of Table I. The d_0 values for Cs^+ and Ba^+ agree very well with r_i, the ionic radius of these ions taken from the literature in the ninth column of Table I. In the case of Na^+ and K^+, however, $d_0 \simeq 2r_i$ and $d_0 \simeq 1.49\ r_i$, respectively. The values of d_0 are used to calculate desorption heats as will be shown shortly.

TABLE I

System	V_0 (volt)	$c\alpha$	μ (D)	d_0 (Å.)	α (10^{24}) calcd.	α (10^{24}) for atom	α (10^{24}) for ion	r_i (Å.)
Cs–W	10.59	1.91	7.87	1.64	7.00	42^a–61^b	2.46^c	1.67^d
K–W	12.86	3.86	9.46	1.97	16.8	46^b	0.88^c	1.33^d
Na–W	12.76	3.10	9.41	1.96	13.4	27^b	0.2^c	0.97^d
Ba–W	10.00	1.90	7.44	1.55	6.58	...	...	1.53^e

[a] J. H. de Boer, *Chem. Weekblad*, **29**, 34 (1932). [b] E. Fues, *Z. Physik*, **82**, 536 (1933). [c] M. Born and W. Heisenberg, *ibid.*, **23**, 388 (1924); J. H. de Boer, "Electron Emission and Adsorption Phenomena," The Macmillan Co., New York, N. Y., 1935. [d] "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1954. [e] Ref. 19 in the text.

We can calculate α, the polarizability of an adsorbate, from the values of $c\alpha$ in Table I, c being calculated from equation 5c. Here use is made of the known values of d_0 just mentioned and $\sigma_m = 3.56 \times 10^{14}/\text{cm.}^2$ which was used by Taylor and Langmuir.[17a] The results are shown in the sixth column of Table I. In the same table, the α values for atoms and for ions from the literature are compared with the calculated α's. One sees that the calculated α's are in between the atomic and ionic polarizabilities.

The maxima in the curves of V *versus* θ are due to the coexistence of atoms with ions at high values of θ. The coexistence is understandable from the potential curves in Fig. 2. At high coverage, curve I for an adsorbed ion is raised considerably so that the transition between the states indicated by I and II (the potential curve for an adsorbed atom) occurs easily. From the deviation between the calculated and observed contact potentials at high coverage, one can calculate the percentage of atoms which coexist with ions. Our calculation shows that the atoms are about 1 ~ 2% at $\theta = 0.9$. Therefore, one may consider that the adsorbed layer in all ranges of θ consists almost entirely of ions.

B. Heat of Adsorption.—The relations between $-\Delta H$ and θ, the heat of *adsorption* and surface coverage, have been observed only for the systems Cs on W[17a] and Na on W.[18a] These data are used for the test of our theory.

a. Heat of Adsorption on a Bare Surface ($-\Delta H_0$).—Using equation 16, we calculate $-\Delta H_0$, the *adsorption* heat on a bare surface. The results are tabulated in Table II, where the values of $e^2/4d_0$ were calculated using the d_0 values which we obtained in Table I. The agreement between the theoretical and experimental values is satisfactory. de Boer[16] has calculated $-\Delta H_0$ for the system Cs on W using equation 16 under the assumption that $d_0 = r_i$. The results are good. Considering that this assumption is not always true, his results are rather fortuitous. In fact, in the case of Na, $d_0 \simeq 2r_i$ as mentioned above. Consequently, the calculation of the $-\Delta H_0$ value under this assumption leads to a value which is more than twice as large as the observed value. As Table II indicates, however, our results for the system Na on W are satisfactory.

TABLE II

System	φ(e. v.)	I(e. v.)	$e^2/4d_0$ (e. v.)	ΔH_0 calcd. (e. v.)	(kcal.)	ΔH_0 obs (e. v.)	(kcal.)
Cs–W	4.52^a	3.88^a	2.19	2.83	65.2	2.94^b	67.8^b
Na–W	4.52^a	5.12^a	1.84	1.24	28.6	1.39^c	32.0^c

[a] Ref. c in Table I. [b] Ref. 17 in the text. [c] Ref. 18 in the text.

b. Variation of Adsorption Heat, $\delta(-\Delta H)$, with Surface Coverage.—The variation $\delta(-\Delta H)$ can be calculated from equation 27, where all the parameters except for d_1 are known from the measurements of contact potentials (*cf.* Table I). We take the d_1 as 6.3 Å. in accordance with Taylor and Langmuir.[17a] The results of the calculations are shown in Fig. 5. The experimental data for the system of Cs on W and Na on W are due to Taylor and Langmuir,[17a] and Bosworth and Rideal,[18a] respectively. The agreement in both cases is satisfactory, no adjustable parameters being used in the calculation except for the factor ν which was taken as $^1/_4$ in both systems.

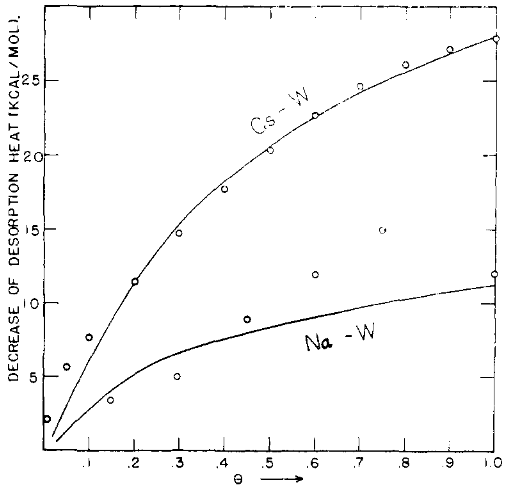

Fig. 5.—Decrease of desorption heat as a function of surface coverage, θ. The full curves indicate the calculated values obtained from equation 27. The experimental points for Cs–W and Na–W were calculated from the data in reference (17a) and (18a), respectively.

c. Variation with Coverage of Activation Free Energy for Desorption.—The rates of desorption of Cs from W and Na from W have been measured by Langmuir[17b] and Bosworth,[18b] respectively. We plot the values of log ($-$d ln θ/dt) for Cs and Na against θ in Figs. 6 and 7. According to equation 14c the slopes of the straight lines in these figures are

[21] M. Boudart, THIS JOURNAL, **74**, 3556 (1952).

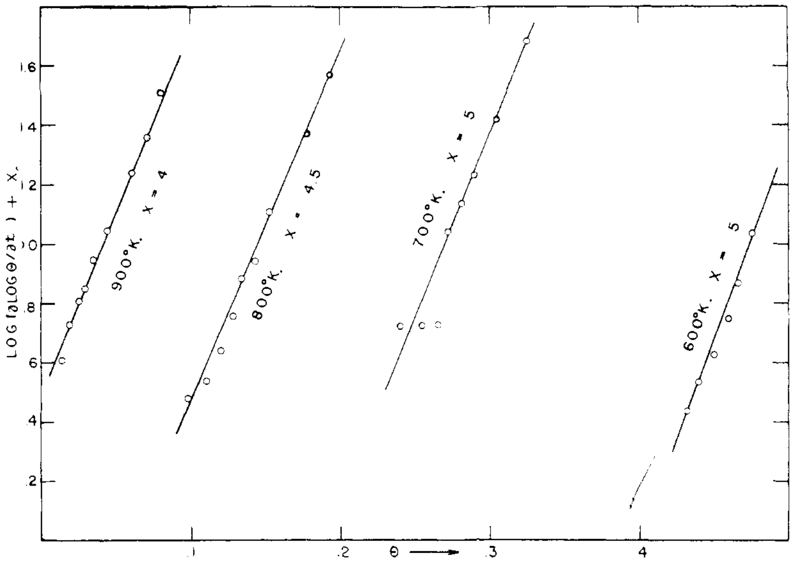

Fig. 6.—The curves of the logarithms of logarithmic desorption rates *vs.* surface coverage, θ, for the system Cs on W. The experimental points were calculated from the θ *vs.* t curves in reference (17b).

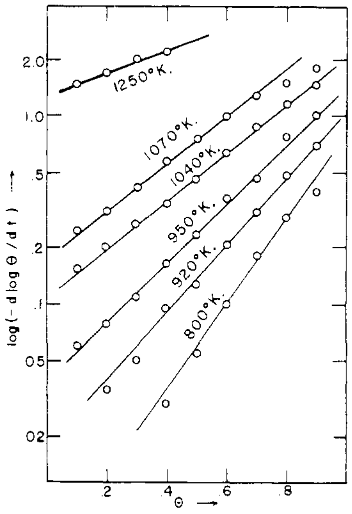

Fig. 7.—The curves of the logarithms of logarithmic desorption rates *vs.* surface coverage, θ, for the system, Na on W. The experimental points were obtained from the logarithmic rates *vs.* θ curves in reference (18b).

$\delta(\Delta F_1^{\ddagger})/RT$ which is equal to b in equation 14a. The intercept at $\theta = 0$ gives the quantity k' which is equal to a of equation 13. From the a's thus obtained at different temperatures, one can obtain $\Delta F_0^{\ddagger}$ using equation 11b. The results are listed in Table III. Eley[13b] has proposed the same formula as our equation 14a, and has calculated the values of b using a part of the Na data.

TABLE III

Cs-W					Na-W				
T °K.	$\Delta F_0^{\ddagger}$, kcal.	$\delta(\Delta F_1^{\ddagger})$, kcal.	b, expt.	b, calcd.	T °K.	$\Delta F_0^{\ddagger}$, kcal.	$\delta(\Delta F_1^{\ddagger})$, kcal.	b, expt.	b, calcd.
600	64.5	43.5	36.6	37.1	800	..	7.41	4.66	3.49
700	65.7	42.0	30.2	31.8	920	63.2	7.48	4.09	3.03
800	67.4	44.4	28.0	27.8	950	63.9	6.84	3.62	2.94
900	69.7	52.7	29.5	24.7	1040	68.0	6.14	2.97	2.69
					1070	68.9	5.81	2.73	2.61

We are now in a position to calculate the quantity b from equation 29. For this purpose, we need to determine the constant, θ_m. In the derivation of equation 29, the condition $c\alpha\theta << 1$ was introduced into (27). Thus, we assume that the critical value of θ, at which $c\alpha\theta$ can be neglected compared to unity, is determined by the condition

$$c\alpha\theta_m = 0.05 \qquad (30)$$

The θ_m values for the systems Cs on W and Na on W are determined from equation 30 using the $c\alpha$ values in Table I. The values of θ_m are 0.0263 and 0.0161, respectively. The calculated and observed values of b are compared in Table III. The agreement between these two values is satisfactory. Thus our theory seems to be established.

Discussion

A. A Second Method for Deriving the $\delta(-\Delta H)$ Formula.—We assume, as before, the presence of an electric double layer of an adsorbate on a surface. Thus $-\Delta H$ (adsorption heat) is given as

$$-\Delta H = I + \frac{c\mu^2\theta}{1 + c\alpha\theta} - e\varphi - \frac{e^2}{4d_0} - \frac{c\mu^2\theta \times c\alpha\theta}{2(1 + c\alpha\theta)^2} + U_i \qquad (31)$$

Here, we ionize an alkali atom at infinite distance from the surface, the work needed being I. The electron thus produced is brought through the field of the double layer to the surface, and is given to the latter. The work needed for bringing the electron through the field is Eed_0 while the energy, $e\varphi$, is liberated when the electron is transferred to the surface. These energies are identically equal to the second and third terms on the right of equation 31. Next, the positive ion produced by the ionization is brought from infinity up to a distance, d_0, from the metal surface. During this process the energy, $e^2/(4d_0)$, due to the image force is liberated, this energy being the fourth term on the right of (31). The adion is polarized by the field, E of the adsorbed layer. The polarization energy is $\alpha E^2/2$ which is exactly the same as the fifth term in equation 31. Besides the image force, the ion experiences other attractive forces. Consequently, the energy, U_i, represented by the last term is liberated. Thus the adsorption heat, $-\Delta H$, is represented by equation 31. The decrease of desorption heat, $\delta(\Delta H)$, is obtained by adding (31) to ΔH_0 which is represented by (16). The result is exactly the same as (27). Our theory is thus seen to be self-consistent.

B. Image Forces.—In our theory we neglect the effect of the electrons coming from adatoms to a metallic surface except for the energies, $e\varphi$, liberated during adsorption. The positive adion induces negative charge at their image distance. This image negative charge is balanced by a distant positive charge which, however, may be thought of as neutralized by the electron contributed by the adatom. Thus, only the positive charges on the adions and their images need to be considered.[22]

C. Entropies of Adions.—From equations 15, 27 and 28, the decrease of activation entropy, $\delta(\Delta S^\ddagger)$ is given as

$$-\delta(\Delta S^\ddagger) = \frac{c\mu^2\theta}{T}\left[\frac{c\alpha\theta(3 + 2c\alpha\theta)}{2(1 + c\alpha\theta)^2} + \frac{1}{4}\ln\left\{\frac{\left(\frac{d_{\rm I}}{r_{\rm i}\sqrt{\theta}}\right)^{1/(1 + c\alpha\theta)}}{d_1/\sqrt{r_{\rm i}^2\theta_{\rm m}}}\right\}\right] \quad (32)$$

In Fig. 8 the full curves are given which were calculated from equation 32 using the parameters obtained previously. The experimental data for calculating $\delta(\Delta S^\ddagger)$ were obtained from the papers of Taylor and Langmuir[17] and Bosworth and Rideal[18] for the systems Cs on W and Na on W, respectively. The agreement between the theory and experiment is reasonably good. One sees from Fig. 8 that the quantity $\delta(\Delta S^\ddagger)$ increases with coverage to a maximum and then decreases. The decrease at high coverage is not prominent in the case of the system Na on W compared to the system Cs on W. We consider below the physical significance of the curves.

The supposition $S_0^\ddagger = S^\ddagger$ may be made, where $S_0^\ddagger$ is the entropy of an activated complex on a bare surface while $S^\ddagger$ is the corresponding quantity on a surface with coverage. This supposition may be justified because according to Fig. 1 the state of the activated complex does not change appreciably with coverage. Thus we have

$$\delta(\Delta S^\ddagger) = \Delta S_0^\ddagger - \Delta S^\ddagger = S_{\rm A} - S_{\rm A(0)} \quad (33)$$

since $\Delta S_0^\ddagger = S_0^\ddagger - S_{\rm A(0)}$, and $\Delta S^\ddagger = S^\ddagger - S_{\rm A}$. Here, $S_{\rm A(0)}$ and $S_{\rm A}$ are the entropies of the adions on a bare surface and on a surface with coverage θ, respectively. The increase of $\delta(\Delta S^\ddagger)$ at low coverage in Fig. 8 indicates, therefore, that the entropy of adions at low concentrations increases with coverage. Physically one can see how adions should first gain entropy as other adions come on to the surface since they gain freedom in the direction normal to the surface due to weakening of the bond. This increase in entropy should continue with increasing coverage until the restriction in the motion parallel to the surface causes an entropy decrease more than compensating for the increase in entropy from the vertical motion.

D. Heterogeneity and Adsorption Heat.—The decrease of adsorption heat with surface coverage has been observed also in other systems.[15,23] The decrease has often been attributed to the "*a priori*" heterogeneity of solid surfaces. It has, however, still been observed with surfaces which ought not to be considered as heterogeneous.[21] Thus, many theories have been proposed to explain the decrease of adsorption heat.[15,24–27] Those theories invariably assume a repulsive potential acting between adsorbed molecules (or atoms). Such a hypothesis, however, is open to question because an excessively large repulsive potential is needed to explain the experimental results. Boudart[21] has assumed an electric double layer of an adsorbate on a surface, as we did in this paper. He assumes the relation,

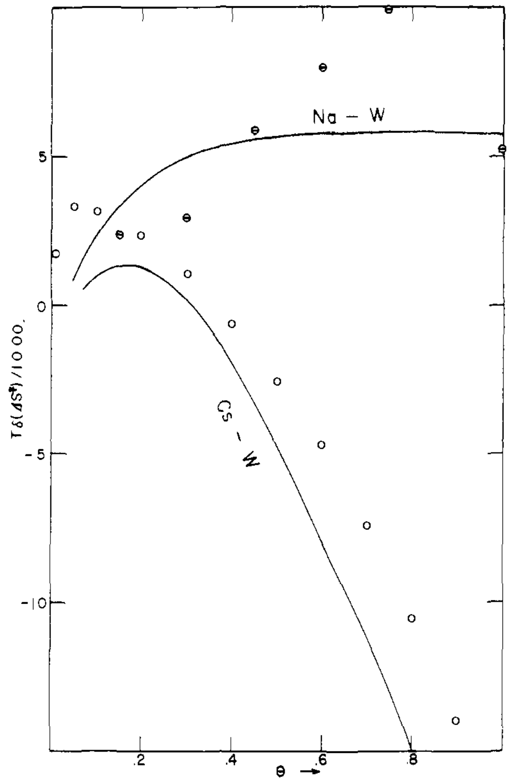

Fig. 8.—Change of activation entropy as a function of surface coverage, θ. The full curves were calculated from equation 32. The experimental points were calculated from the data in reference (17a, b) and (18a, b).

$$\delta(-\Delta H) = \frac{n}{2}Ve \quad (34)$$

where n is the number of valence electrons participating in chemisorption. Using this relation, he explains many experimental results. Kemball[11b] has pointed out the defects of his theory, and we have found equation 34 holds only for a special value of θ. In fact, the relation between $\delta(-\Delta H)$ and V, and consequently also of θ, is not as simple as (34). Equation 27 is better as attested by the agreement between theory and experiment in Fig. 5. Boudart's ideas embodied in his theory[21] of "induced heterogeneity," however, is still substantially correct as has been shown by its extension in our paper. We plan to apply our theory to the adsorption of gases on metals.

Acknowledgment.—We wish to express our appreciation to California Research Corporation for the financial support.

SALT LAKE CITY, UTAH

---

[22] In treating image charges, the metallic medium between the adions and images is considered as though it were filled with the nonmetallic medium (*cf.* Slater and Frank, "Introduction to Theoretical Physics," McGraw-Hill Book Co., New York, N. Y., 1933, pp. 215–216).

[23] O. Beeck, "Advances in Catalysis," Vol. 2, Academic Press, Inc., New York, N. Y., 1950, pp. 171–193.

[24] J. K. Roberts, "Some Problems in Adsorption," Cambridge Univ. Press, Cambridge, England, 1939.

[25] R. Peierls, *Proc. Camb. Phil. Soc.*, **32**, 471 (1936).

[26] J. S. Wang, *Proc. Roy. Soc.* (*London*), **A161**, 127 (1937).

[27] S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1942, pp. 363–366.