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

# Adsorption Kinetics. II. Nature of the Adsorption Bond[1]

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One may expect three types of chemisorptions: pure ionic, pure covalent and mixed types. Let us suppose the surface complex M–A, formed by chemisorption of an adsorbate A on an adsorbent M, forms a diatomic molecule. Then the ionic character (fraction) $C_i^2$ of the adsorption bond M–A is given by $1/C_i^2 = 1 + (E - H_{ii})/(E - H_{cc})$ (eq. 1). Here $E$ is the bond energy of M–A, $H_{ii}$ and $H_{cc}$ are the energies of the pure ionic and pure covalent bonds, respectively. $C_i^2$ is calculated from $\mu' = C_i^2 e r_{MA}$ (eq. 2), where $\mu'$ and $r_{MA}$ are the dipole moment and the bond length of M–A. Since we can calculate $H_{ii}$ and $H_{cc}$ semi-empirically, $E$ is calculated from eq. 1 and 2. Thus, the desorption heat from a nearly bare surface is calculated. The calculated and observed desorption heats are compared for the systems Ba on W, Sr on W, and the diatomic gases ($H_2$, $O_2$, $N_2$, CO) on metals (W, Ni, Fe, Ta, Rh, Cr, Cu, Pt). The agreement is satisfactory. From the results we conclude: (1) The adsorption bonds of the systems, Cs on W, Na on W, are purely ionic. (2) The bonds, Ba–W, Cs–W, are ionic with small amount of covalent character ($C_i^2 = 0.97$ for Ba, $C_i^2 = 0.67$ for Sr). (3) The bonds of the systems, gases on metals, are covalent with small amount of ionic character ($C_i^2 = 0.02$ to 0.09). The Becker–Zeldovich equation for desorption, $-d\theta/dt = a\theta \exp(b\theta)$ (eq. 3), holds for the desorption rates of the systems, Ba on W, Sr on W, and oxygen on W. In eq. 3, $\theta$ is the surface coverage, $a$ and $b$ are constants. The activation heat for desorption and heat of desorption (adsorption) decrease with $\theta$ generally. This fact is explained as being due to the field of the adsorbed layer on the desorbing atom.

## I. Introduction

Generally it is understood that chemisorption accompanies electron transfer between adsorbates and adsorbents. Thus, the bonds between these two are chemical in nature. As there are ionic, homopolar and mixed-type bonds in molecules, one expects the presence of the corresponding three types of bonds in adsorption. We study in this paper the nature of the "adsorption bonds."

If we approximate the surface complex formed between a surface atom and an adatom to a diatomic molecule, it is possible to calculate the percentage of ionic characters in the adsorption bond using the theories of Wall[2a] and Ree and Muroyama.[2b] Provided that the ionic percentage is known, the bond energy is calculated as Ree and Muroyama[2b] did for diatomic molecules. Thus we can calculate the heat of desorption from a nearby bare surface, since the latter is closely connected to the energy of the adsorption bond.

We also consider the changes of desorption heat and of activation heat for desorption with surface coverages. Both changes are caused by the effect of an adsorbed layer on the desorbing atoms and molecules. Thus, the investigation of the change of desorption heat and activation heat with surface coverages elucidate the nature of the adsorption bond.

## II. Theory of Chemisorption on Metallic Surfaces

**A. The Energy of the Adsorption Bond.**—During the last few decades, quantum mechanics has made great strides in the physics of solids. Thus, the physical properties, such as electric conduction,[3] cohesive force,[3] hardness,[4] density[4] and mechanical strength,[5] are successfully explained. Likewise, the studies of metallic surfaces have been greatly developed.[6–9] However, the general theory of the behavior of surface atoms is still imperfectly understood.

We may assume the presence of unpaired electrons for the surface atoms, M. Thus, the latter interact with an adsorbate, A, making a surface complex, M–A. The fraction, $C_i^2$, of the ionic bond in the adsorption bond is given by[2b]

$$\frac{1}{C_i^2} = 1 + \frac{E - H_{ii}}{E - H_{cc}} \qquad (1)$$

Here, $E$ is the energy of the adsorption bond, $H_{ii}$ and $H_{cc}$ are the energies for ideal ionic and covalent bonds, respectively.[10] To a good first-order approximation, the $H_{ii}$ and $H_{cc}$ are represented by the equations

$$H_{ii} = A_0 - I + \frac{8}{9}\frac{e^2}{r_{MA}} \qquad (2)$$

$$H_{cc} = \{E(\text{M–M}) + E(\text{A–A})\}/2 \qquad (3)$$

Here, $A_0$ and $I$ are the electron affinity of M and the ionization potential of A, respectively, if the electron transfer occurs from A to M. (When the direction of the electron transfer is reversed, $A_0$ is the electron affinity of A, while $I$ is the ionization potential of M.) $r_{MA}$ is the distance between the atoms, M and A. $E$(M–M) and $E$(A–A) are the bond energies of the single bonds, M–M and A–A, respectively. $e$ is the electronic charge $4.80 \times 10^{-10}$ e.s.u.[11] The bond moment, $\mu'$, is expressed by

$$\mu' = C_i^2 e r_{MA} \qquad (4)$$

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[1] Presented before the Division of Physical and Inorganic Chemistry of the 130th American Chemical Society meeting at Atlantic City, New Jersey, September 19, 1956.

[2] (a) F. T. Wall, THIS JOURNAL, **61**, 1051 (1939); (b) T. Ree (Ri) and N. Muroyama, *Proc. Imp. Acad. Japan*, **20**, 93 (1944); *C. A.*, **43**, 5240 (1949).

[3] F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., New York, N. Y., 1940.

[4] L. Pauling, *Proc. Roy. Soc.* (*London*), **A196**, 343 (1949).

[5] W. Shockley, "Imperfections in Nearly Perfect Crystals," John Wiley and Sons, Inc., New York, N. Y., 1952.

[6] K. Huang and G. Wyllie, *Disc. Faraday Soc.*, **8**, 18 (1950).

[7] C. A. Coulson and G. R. Baldock, *ibid.*, **8**, 27 (1950).

[8] R. Gomer and C. S. Smith, "Structure and Properties of Solid Surfaces," The University of Chicago Press, Chicago, Ill., 1953.

[9] W. E. Garner, "Chemistry of the Solid State," Academic Press, Inc., New York, N. Y., 1955.

[10] Equation 1 is obtained readily by solving the wave equation, $H\psi = E\psi$. Here $\psi$ is an eigenfunction of the adsorption bond, represented by $\psi = C_i\psi_i + C_c\psi_c$, where $\psi_i$ and $\psi_c$ are the eigenfunctions of the ideal ionic and covalent bonds, respectively, and $C_i$ and $C_c$ are constants. The quantities, $H_{ii}$ and $H_{cc}$, are, $H_{ii} = \int \psi_i H \psi_i d\tau$, $H_{cc} = \int \psi_c H \psi_c d\tau$.

[11] The bonding energy, $W$, between a positive and negative ion separated a distance, $r$, is given by $W = -e^2/r + br^{-9}$. At equilibrium distance, $r_{MA}$, where the energy of the system is minimum, the energy is represented by $W_e = (8/9)e^2/r_{MA}$. This is the last term on the right of eq. 2. Equation 3 is Pauling's equation (*cf.* reference 12, p. 48).

Ree and Muroyama[2b] calculated bond moments applying eq. 1 to 4 for 16 diatomic molecules and 16 single bonds in polyatomic molecules with good agreement with experiment. Thus, the applicability of Equations 1 to 4 seems ascertained. According to Pauling[12] the following approximation holds

$$E = H_{cc} + 23.06(X_M - X_A)^2 \tag{5}$$

Here, $X_M$ and $X_A$ are the electronegativities of M and A, respectively. When $X_M - X_A$ is small, the following approximation also applies

$$E = H_{cc} + 23.06(\mu')^2 \tag{6}$$

where $\mu'$ is the bond moment of the bond, M–A.

Next we consider the relation between the bond energy, $E$, and $\Delta H_0$, the desorption heat from a nearly bare surface. For the desorption of monoatomic gases, $E$ is $\Delta H_0$ itself, *i.e.*

$$\Delta H_0 = E \tag{7}$$

If homonuclear diatomic gases adsorb dissociatively, but desorb as molecules, $\Delta H_0$ is given by

$$\Delta H_0 = 2E - E(\text{A–A}) \tag{8}$$

**B. Pure Ionic and Pure Homopolar Bonds.**—Equation 1 indicates that when the adsorbate is in an ionic state (*i.e.*, $C_i^2 = 1$) then $\Delta H_0$ of a monoatomic gas is given by 2. In our paper I,[13] we have shown that Cs and Na are adsorbed in the ionic state on tungsten, and that $\Delta H_0$ is represented by

$$\Delta H_0 = e\varphi - I + \frac{e^2}{4d_0} \tag{9}$$

Here, $\varphi$ is the work function of tungsten, $d_0$ is the distance of the adion from the W surface, the latter being assumed to be a smooth continuum. By comparing eq. 2 with 9, we see they are equivalent. Thus, in the case of ionic adsorption, the classical electrostatical treatment developed in paper I is valid.

From eq. 1 one sees that $E = H_{cc}$ if $C_i^2 \simeq 0$, *i.e.*, the latter condition represents a homopolar adsorption. According to Mignolet,[14] even in the case where van der Waals adsorption would prevail, the adsorbate shows a contact potential. This is explained by assuming a small amount of electron transfer or the polarization of the adsorbate due to a surface field. In any case, a pure homopolar adsorption will not be so important in chemisorptions, since the latter accompany electron transfer more or less.

**C. Variation of Contact Potentials and of Desorption Heats with Surface Coverage $\theta$.**—In paper I, the contact potential, $V$, was given by the Helmholtz equation

$$V = \frac{4\pi\sigma_m e d_0\theta}{\epsilon} = \frac{V_0\theta}{1 + C\alpha\theta} = \frac{4\pi\sigma_m\mu_0\theta}{1 + C\alpha\theta} \tag{10}$$

where

$$V_0 = 4\pi\sigma_m e d_0 \tag{11a}$$

$$C = 4\pi\sigma_m/d_0 \tag{11b}$$

$$\mu_0 = e d_0 \tag{12}$$

Here, $\epsilon$ is the dielectric constant of the medium in the electric double layer formed by an adsorbed film; $\sigma_m$ is the number of adsorption sites per unit area; $\alpha$ is the polarizability of the adion; as already defined, $d_0$ is the distance indicated in Fig. 1A, where an ionic adsorption is shown.

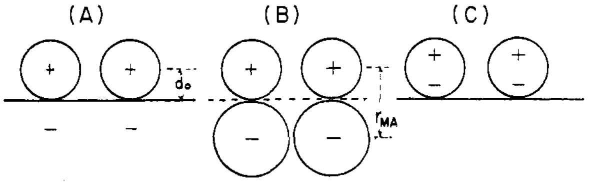

Fig. 1.—(A) ionic adsorption. The negative charges are the electrical mirror images of the positive charges of the adions. (B) covalent adsorption with ionic character. Here an example is shown, where adatoms are charged positively while the adsorbent atoms are negatively charged. (C) van der Waals adsorption. The adatoms ("admolecules") are polarized by a surface field.

The Helmholtz equation holds also for the electric double layer formed by covalent chemisorption.[15] Thus $V$ in this case is given by

$$V = 2\pi\sigma_m\mu'\theta \tag{13}$$

Here $\mu'$ is the moment of the dipole shown in Fig. 1B, and is given by 4. Equation 13 is readily obtained from 10 by substituting $\mu'$ for $2\mu_0$ (the dipole moment in the ionic adsorption) and unity for $\epsilon$.

Next, we consider the decrease of desorption heat, $\delta(\Delta H)$, with surface coverage $\theta$. Here we neglect $\delta(\Delta H)$ due to the surface heterogeneity of adsorbents. In paper I, we derived the equation

$$\delta(\Delta H) = \frac{C\mu_0^2\theta}{1 + C\alpha\theta}\left\{1 - \frac{C\alpha\theta}{2(1 + C\alpha\theta)}\right\} - \frac{C\mu_0^2\theta}{1 + C\alpha\theta}\left\{{}^1/_4 \ln \frac{d_1}{r_i\sqrt{\theta}}\right\} \tag{14a}$$

(The right-hand side of eq. 14a expresses also the decrease of adsorption heat, $\delta(-\Delta H)$, with surface coverage, $\theta$.) In eq. 14a, $d_1$ is the distance between two neighboring adions at $\theta = 1$, and $r_i$, the radius of the adion. The first term on the right of (14a) is the energy liberated when an adion desorbs from the surface with coverage $\theta$. The

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[12] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 60.

[13] I. Higuchi, T. Ree and H. Eyring, THIS JOURNAL, **77**, 4969 (1955).

[14] J. C. P. Mignolet, *Disc. Faraday Soc.*, **8**, 105 (1950); *Rec. trav. chim., Pays-Bas*, **74**, 685 (1955).

[15] When dipoles with a small moment, $\mu'$, arrange vertically on a metallic surface, as shown in Fig. 1C, the contact potential is represented by $V = 4\pi\sigma_m\mu'\theta$. In the cases of A and B in Fig. 1, however, the contact potentials are both represented by $2\pi\sigma_m\theta\mu'$ (*cf.* eq. 13). In the literature, both equations $V = 4\pi\sigma_m\theta\mu'$ and $V = 2\pi\sigma_m\theta\mu'$, are used. The latter was proposed by Langmuir,[16a] and used by Bosworth and Rideal,[16b] and Eley.[17] However, Becker,[18] de Boer[19] and Moore and Allison[20] use $V = 4\pi\sigma_m\theta\mu'$. In his recent paper, Eley[21] uses the equation with the factor, $4\pi$. There is an argument concerning which of the two equations is right.[20] We believe, however, that the application of these equations is different according to the mechanisms of adsorption.

[16] (a) I. Langmuir, THIS JOURNAL, **54**, 2798 (1932); *Phys. Rev.*, **44**, 423 (1933); (b) R. C. L. Bosworth and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A162**, 1, 32 (1937).

[17] D. D. Eley, *Disc. Faraday Soc.*, **8**, 34 (1950).

[18] J. Becker, "Advances in Catalysis," Vol. 7, Academic Press, Inc., New York, N. Y., 1955.

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

[20] G. E. Moore and H. W. Allison, *J. Chem. Phys.*, **23**, 1609 (1955).

[21] D. D. Eley, "Catalysis and the Chemical Bond," Vol. VII, The P. C. Reilly Lectures in Chemistry, University of Notre Dame, 1954.

second term is the extra-energy, $U_i$, to overcome the forces between the representative adion and the image charges of other adions. If $C\alpha\theta << 1$ and $U_i$ is very small, eq. 14a becomes

$$\delta(\Delta H) = C\mu_0^2\theta = 2\pi\sigma_m e\mu'\theta \tag{14b}$$

We assume 14b is applicable to covalent adsorption. Here $\mu' = C_i^2 e r_{MA}$, and the conditions, $C\alpha\theta < < 1$ and $U_i$ very small, are satisfied. Substituting 13 into 14b one obtains

$$\delta(\Delta H) = eV \tag{15a}$$

Equation 15a is also obtained directly from 13 through the following considerations: the potential $V$ is formed by an electron-transfer accompanying the covalent adsorption. Thus, in the desorption of an adatom, the electron transferred is moved back to the original position through the potential $V$. Thus the desorption heat decreases by $eV$, since the potential favors the desorption. If homonuclear diatomic molecules chemisorb dissociatively, but desorb as molecules, the following relation holds

$$\delta(\Delta H) = 4\pi\sigma_m\mu' e\theta = 2eV \tag{15b}$$

In the literature,[22-24] eq. 15a has been used to explain the decrease of desorption (adsorption) heats with $\theta$. We will here apply 15b to explain the curves of $\delta(\Delta H)$ *vs.* $\theta$ for various cases.

**D. Kinetics of Chemisorption.**—The Becker–Zeldovich equations[13] for the rates of adsorption and desorption are, respectively

$$\frac{d\theta}{dt} = a(1 - \theta)e^{-b\theta} \tag{19}$$

$$-\frac{d\theta}{dt} = a\theta e^{b\theta} \tag{20}$$

In paper I, we clarified the physical significance of the constants, $a$ and $b$. That is, they are represented by the equations

$$a = (kT/h)\exp(-\Delta F_0^{\ddagger}/RT) \tag{21}$$

and

$$b = \delta(\Delta F_1)/RT \tag{22}$$

where

$$\delta(\Delta F_1^{\ddagger}) = C\mu_0^2\left(1 - {}^1/_4 \ln\frac{d_1}{r_i\sqrt{\theta_m}}\right) \tag{23}$$

Here, $\Delta F_0^{\ddagger}$ is the activation free energy of desorption (adsorption) when $\theta \simeq 0$; $\delta(\Delta F_1^{\ddagger}) = \Delta F_0^{\ddagger} - \Delta F_1^{\ddagger}$, where $\Delta F_1^{\ddagger}$ is the activation free energy at $\theta = 1$; $\theta_m$ is a small constant which satisfies the condition, $C\alpha\theta_m << 1$. We consider here the kinetics of desorption of chemisorbed atoms due to covalent forces.

**1. Potential Curves.**—The profile of the potential surface for desorption (adsorption) is shown in Fig. 2. Curve I is the potential curve for the atom chemisorbed; curve II is for the adsorbate, which is an atom or a molecule, adsorbed by van der Waals forces. Thus, the desorption occurs when an adatom in the state indicated by Curve I changes to the state corresponding to curve II. $\Delta H_0^{\ddagger}$ is the activation heat for desorption at $\theta \simeq 0$, whereas $\Delta H^{\ddagger}$ is the activation heat at coverage $\theta$. $\Delta H_0$ and $\Delta H$ are the desorption heats at $\theta \simeq 0$ and at coverage, $\theta$, respectively. In Fig. 2, the case is shown where the adsorption occurs instantaneously, *i.e.*, the activation heat for the adsorption is nearly zero regardless of $\theta$. Thus, we have the relations

$$\Delta H_0^{\ddagger} = \Delta H_0 \tag{24a}$$

$$\Delta H^{\ddagger} = \Delta H \tag{24b}$$

$$\delta(\Delta H^{\ddagger}) = \delta(\Delta H) \tag{24c}$$

where $\delta(\Delta H^{\ddagger}) = \Delta H_0^{\ddagger} - \Delta H^{\ddagger}$. If curve II represents the state of an adsorbed diatomic molecule, $D$ in Fig. 2 signifies the dissociation energy. However, if curve II indicates the state for the atom adsorbed by van der Waals forces, $D$ will be zero.

It is appropriate to mention here the reason why the potential curve at coverage $\theta$ (the dashed curve) is shifted as shown in Fig. 2. As in paper I, the shift is due to the effect of a double layer on the chemisorbed atom, *i.e.*, the field of the layer opposes the formation of adsorption bond. Thus, $\Delta H$ and $\Delta H^{\ddagger}$ decrease with $\theta$. The amount of $\delta(\Delta H)$ and $\delta(\Delta H^{\ddagger})$ are given by $eV$ for the reason already mentioned.

**2. Activation Free Energy for Desorption.**—In covalent adsorption, eq. 23 is written as

$$\delta(\Delta F_1^{\ddagger}) = 2\pi\sigma_m e\mu'\left(1 - {}^1/_4 \ln\frac{d_1}{r_i\sqrt{\theta_m}}\right) \tag{25a}$$

The second term in the parentheses on the right of eq. 25a is due to image forces. Thus, it can be neglected when the ionic character of adsorption bonds is very small. Thus, $\delta(\Delta F_1^{\ddagger})$ is given by

$$\delta(\Delta F_1^{\ddagger}) = 2\pi\sigma_m e\mu' = eV_1 \tag{25b}$$

where $V_1$ is the contact potential at $\theta = 1$ (*cf.* eq. 13). It is also true that in covalent chemisorption with weak ionic character $\delta(\Delta S^{\ddagger})$ at coverage $\theta$ is nearly zero regardless of $\theta$, *i.e.*

$$\delta(\Delta S^{\ddagger}) = \Delta S_0^{\ddagger} - \Delta S^{\ddagger} = 0 \tag{26}$$

where, $\Delta S_0^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activation entropies at $\theta \simeq 0$ and at $\theta$, respectively. From eqs. 24 and 26, we obtain the relations

$$\delta(\Delta F_1^{\ddagger}) = \delta(\Delta H_1^{\ddagger}) = \delta(\Delta H_1) \tag{27}$$

where $\delta(\Delta H_1^{\ddagger}) \equiv \Delta H_0^{\ddagger} - \Delta H_1^{\ddagger}$. The subscripts, 0 and 1, indicate that the attached quantities are measured at $\theta \simeq 0$ and $\theta = 1$.

## III. Applications

**A. Adsorption of Strontium and of Barium on Tungsten.**—Recently, Moore and Allison[20] have reported the results of their studies on the adsorption of Sr and Ba on W. These systems are very interesting from a theoretical viewpoint, as will be seen shortly. Moore and Allison[20] measure the work function $\varphi$ by determining the tungsten filament temperatures, $T$ and $T_0$, which yielded a given electron emission from a covered and from a bare tungsten surface, respectively. That is, $\varphi$ is calculated from the equation

$$\varphi = \frac{\varphi_0}{T_0}T + 2\frac{kT}{e}\ln\frac{T}{T_0} \tag{28}$$

where $\varphi_0$ is the work function for the bare surface. We calculate the contact potential, $V$, which is

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[22] M. Boudart, THIS JOURNAL, **74**, 3556 (1952). He assumes, however, the relation $\delta(\Delta H) = eV/2$.

[23] C. Kemball, "Annual Review of Physical Chemistry," Vol. 4, Annual Reviews, Inc., Stanford, California, 1953, p. 309. Kemball discusses the relation $\delta(\Delta H) = eV/2$.

[24] J. C. P. Mignolet, *J. Chem. Phys.*, **23**, 753 (1955).

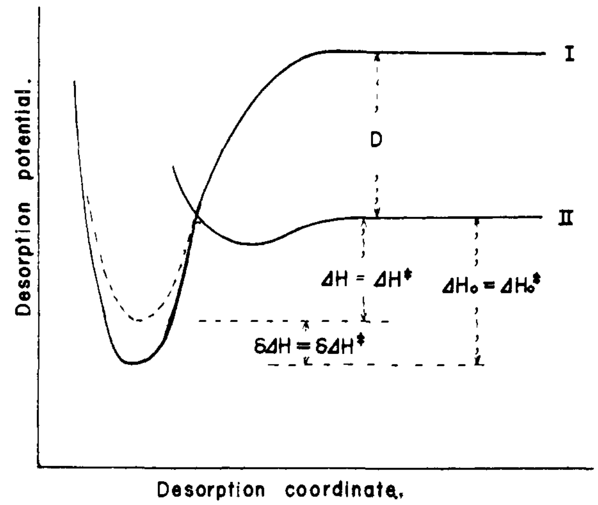

Fig. 2.—Potential diagram for desorption. The dashed potential curve indicates the potential shift due to the field of the adsorbed layer.

equal to $\Delta\varphi = \varphi_0 - \varphi$, from 28 using the curves of $T$ *vs.* $\theta$ obtained by Moore and Allison.[20] The results are shown by circles and dots in Fig. 3. Using eq. 10, the parameters $V_0$ and $C\alpha$ were determined so that 10 fixes the experimental points best. The full curves in Fig. 3 are recalculated from eq. 10 using the parameters, $V_0$ and $C\alpha$, given in Table I. In the calculations, the value, $\sigma_m = 4.89 \times 10^{14}/\text{cm.}^2$, was used, which is the surface density of adsorption sites on the surface [100], and was experimentally determined by Moore and Allison.[20]

TABLE I

| | $V_0$ (v.) | $C\alpha$ | $\alpha \times 10^{24}$ | $d_0$ (Å.), obsd. | $r_i$ (Å.), ref. | $\mu_0$ ($D$) | $\Delta H_0$ (kcal.), obsd. | $\Delta H_0$ (kcal.), calcd. |
|---|---|---|---|---|---|---|---|---|
| Sr on W | 8.0 | 2.4 | 3.53 | 0.90 | $1.32^a$ | 4.34 | $75 \sim 82^b$ | $65.2^c$ |
| Ba on W | 12.5 | 3.1 | 7.13 | 1.41 | $1.53^a$ | 6.77 | $80 \sim 86^b$ | $43.2^c$ |

[a] Reference 12, p. 346. [b] Reference 20. [c] Calculated from eq. 9. The value of $\varphi$ for W is 104.2 kcal., $I = 131.2$ kcal. for Sr, and $I = 120.1$ kcal. for Ba.

Using the values of $V_0$ and $C\alpha$, the parameters, $\mu_0$, $d_0$ and $\alpha$ in Table I were calculated from eq. 11a to 12. The heats of desorption, $\Delta H_0$, were calculated from eq. 9, and are compared with the observed $\Delta H_0$'s[20] in Table I. One sees that the agreement is not especially good. In the same table, the values of $d_0$ are compared with $r_i$'s for the radii of the respective ions, taken from the reference shown thereon. One sees that $d_0 < r_i$. This result is unlikely if the adsorption bonds are purely ionic, since in ionic adsorptions the relation, $d_0 \geq r_i$, holds (*cf.*, paper I). Because of the improbability of the result $d_0 < r_i$, we give up the treatment of the systems, Sr on W and Ba on W, as pure ionic adsorptions.

We calculate $C_i^2$ from eq. 4 using the values of $\mu'$ ($= 2\mu_0$) found experimentally. The values of $C_i^2$ for the systems, Ba on W and Sr on W, are 0.974 and 0.672, respectively. Thus, we find that the ionic character of the adsorption bonds in these cases is not 100% (*i.e.*, $C_i^2 \neq 1$) as it was in the cases treated in paper I.[25] But still it is very large compared to the systems, oxygen on W and hydrogen on W (*cf.* below). Thus, the adsorption bonds in the systems, Sr on W and Ba on W, are in between ionic and covalent adsorption. The adsorption heats of Sr and of Ba on W are calculated from eq. 1 and 7 by the procedures mentioned below, and are tabulated in Table II with the other results obtained.

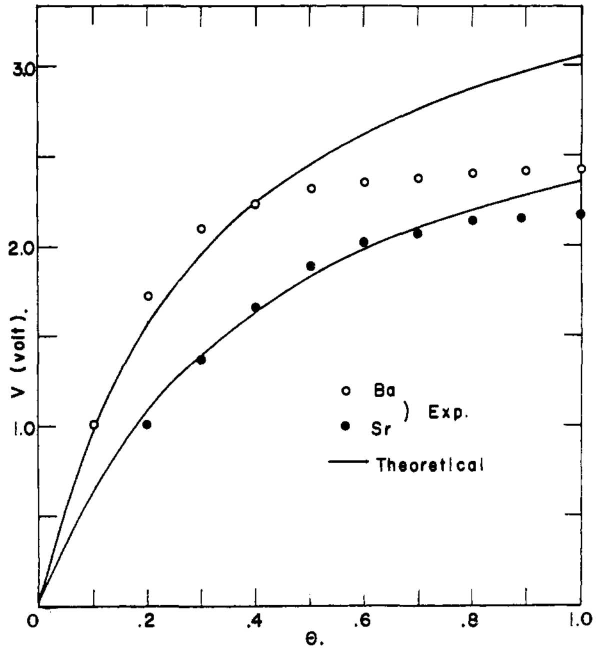

Fig. 3.—Contact potential *versus* surface coverage. The theoretical curves are calculated from eq. 10.

**B. Calculations of Chemisorption Heats.**—The fraction of ionic bond, $C_i^2$, in adsorption is calculated from eq. 4 using the experimental values of $\mu'$, which were obtained from the measurements of contact potentials (*cf.* eq. 13). The bond energies of the systems, adsorbates on metals, were calculated using eq. 1, and the chemisorption heats were calculated from eq. 7 and 8 for monoatomic and diatomic gases, respectively. The results are shown in Table II. The first column indicates the adsorption systems; the necessary data in the calculations are tabulated from the second to the seventh column. In the ninth and tenth columns, the calculated and observed heats are compared. The source of all the data listed in Table II is shown in the appendix to this table.

In Table II, the values of $r_{\text{MA}}$ are the atomic radii of the metallic adsorbents plus the covalent bond radii of adatoms, except as otherwise indicated. The bond energy, $E(\text{M–M})$, of a molecule, M–M, which is a hypothetical diatomic molecule of a metal, are obtained by multiplying the vaporization heat of the metal, $\lambda$, by a factor, $\chi$, *i.e.*, $E(\text{M–M}) = \chi\lambda$. $\chi$ is $^2/_{12}$ for face-centered cubic metals, $^2/_8$ for body-centered cubic, because in the former each atom has 12 nearest neighbors while in the latter it has 8 nearest.

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(25) It is interesting to note that $2\mu_0$ for the system, Ba on W, in Table I is nearly equal to the value of $2\mu_0$ in paper I. As the figure, $C_i^2 = 0.974$, indicates, the system, Ba on W, is nearly ionic.

TABLE II[a]

| System M,A | $\mu'$ (*D*) | $r_{MA}$ (Å.) | *E*(M–M) | *E*(A–A) | *I*(kcal.) | $A_0$(kcal.) | *E*(kcal.) | $\Delta H_{0\text{calcd.}}$ (kcal.) | $\Delta H_{0\text{exp.}}$ (kcal.) |
|---|---|---|---|---|---|---|---|---|---|
| W,Ba | 13.54 | 2.90[f] | 54.4 | 22.7 | 120.1 | 104.2[j] | 87.0 | 87.0 | 83[m,n] |
| W,Sr | 8.68 | 2.69[f] | 54.4 | 15.3 | 131.2 | 104.2[j] | 128.1 | 128.1 | 79[m,n] |
| W,H | 0.460[b] | 1.67 | 54.4 | 103.4 | 183.9 | 16.4[k] | 83.5 | 63.6 | 45[p] |
|  | .212[b] | 1.67 | 54.4 | 103.4 | 183.9 | 16.4[k] | 80.9 | 58.4 |  |
| Ni,H | .183[c] | 1.47[g] | 15.1 | 103.4 | 176.1 | 16.4[k] | 59.8 | 16.2 | 31[q] 27[r] |
| Fe,H | (0.141) | 1.56 | 22.7 | 103.4 | 181.2 | 16.4[k] | 63.9 | 24.4 | 32[s] 19[r] |
| Ta,H | ( .46) | 1.74 | 46.3[h] | 103.4 | (183.9) | 16.4[k] | 79.4 | 55.4 | 39[t] |
| Rh,H | ( .46) | 1.64 | (18.5) | 103.4 | 177.5 | 18.4[k] | 63.8 | 24.2 | 28[t] |
| Cr,H | ( .46) | 1.55 | 19.1 | 103.4 | 155.8 | 16.4[k] | 62.0 | 20.6 | 44[t] |
| Cu,H | ( .46) | 1.57 | 18.6 | 103.4 | 178.0 | 16.4[k] | 63.4 | 23.4 | 35[u] 9[v] |
| Co,H | ( .46) | 1.56 | 15.1 | 103.4 | 181.5 | 16.4[k] | 61.8 | 20.2 | 19[r] |
| Pt,H | ( .46) | 1.68 | 20.7 | 103.4 | 207.5 | 16.4[k] | 67.1 | 30.8 | 32[v] 18[r] |
| W,O | .778[d] | 1.92 | 54.4 | 118.2/2[i] | 183.9 | 50.7[k] | 117.2 | 116.2 | 150[p] 139[v] |
| Ni,O | ( .778) | 1.78 | 15.1 | 118.2/2[i] | 175.9 | 50.7[k] | 73.8 | 29.4 | 130[q] |
| Fe,O | ( .778) | 1.81 | 22.7 | 118.2/2[i] | 181.2 | 50.7[k] | 82.7 | 47.2 | 71[s] |
| W,N | .610[e] | 1.917 | 54.4 | 225.1/3[i] | 183.9 | 1[k] | 201.4 | 177.7 | 32[e] 75[w] 95[q] |
| Ta,N | ( .610) | 1.967 | 46.3 | 225.1/3[i] | (183.9) | 1[k] | 189.0 | 152.9 | 135[x] |
| Fe,N | ( .610) | 1.807 | 22.7 | 225.1/3[i] | 181.2 | 1[k] | 152.0 | 78.9 | 40[q] 70[s] |
| Ni,CO | ( .610) | 2.01 | 15.1 | 58.6 | 176.1 | 31.6[k] | 51.1[l] | 51.1 | 35[q] |
| Fe,CO | ( .610) | 2.03 | 22.7 | 58.6 | 181.2 | 31.6[k] | 55.5[l] | 55.5 | 32[s] |

[a] The bond energy, *E*(M–M), is calculated from $E(\text{M–M}) = \chi\lambda$, where $\lambda$ is the vaporization heat of a metal, $\chi = 1/6$ for face-centered cubic metals, *e.g.*, Sr, Ni, Rh, Cu, Co, Pt and $\chi = 1/4$ for body-centered metals, *e.g.*, W, Ba, Fe, Ta, Cr, etc. All the values of $\lambda$, except for tantalum, are obtained from the "International Critical Tables," Vol. I, McGraw–Hill Book Co., New York, N. Y., 1926, p. 102. Unless otherwise mentioned, the values of *E*(A–A) are taken from Pauling's book (ref. 12, p. 53 and 130). Except where otherwise indicated, $r_{MA} = r_A + r_M$. Here $r_M$ is the atomic metal radius (*cf.* "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1954), and $r_A$ is the covalent bond radius of the adsorbed atom (*cf.* ref. 12, p. 164–187). All the ionization potentials are taken from I. G. H. Herzberg, "Atomic Spectra and Atomic Structure," 2nd. ed., Dover Publications, Inc., New York, N. Y., 1944, p. 200. The numbers in the parentheses for $\mu'$, *E*(A–A), or *I* indicate that the quantities have been estimated by interpolation or estimation. [b] The values 0.460 and 0.212 were calculated from eq. 13 using the value of 1.04 and 0.48 v. for $V_1$, obtained by Bosworth (*cf.* ref. 27) and by Mignolet (*cf.* ref. 24), respectively, where $\sigma_m = 1.2 \times 10^{15}$. [c] Calculated from eq. 13 using the values, $V_1 = 0.345$ v. and $\sigma_m = 1.47 \times 10^{15}$, the former value was obtained by Mignolet (*cf.* ref. 14). [d] Calculated from eq. 13 using the values, $\sigma_m = 1.2 \times 10^{15}$ and $V_1 = 1.76$ v., the latter was obtained by Bosworth and Rideal (*cf.* ref. 34). [e] Calculated from eq. 13 using the values, $\sigma_m = 1.2 \times 10^{15}$ and $V_1 = 1.38$ v. The latter was obtained by Bosworth (*cf.* ref. 28). [f] In these cases, the ionic character of the adsorption bonds is large. Thus, we use 1.53 Å. for Ba and 1.32 Å. for Sr; these values are the monovalent ionic radii of the corresponding elements (ref. 12) p. 346). [g] Landolt-Börnstein, "Physikalische-Chemische Tabellen," 6th ed., Vol. I, 1923, p. 25. [h] D. B. Langmuir and L. Malter, *Phys. Rev.*, **55**, 1138 (1938). [i] 118.2 and 225.1 kcal. are the dissociation energies of $O_2$ and $N_2$, respectively, *cf.* K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948). [j] This value is the work function of tungsten, 4.52 *eV* (M. Born and W. Heisenberg, *Z. Physik*, **82**, 536 (1933)). [k] A. C. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Dover Publications, Inc., New York, N. Y., 1950, p. 93. [l] The chemisorption of carbon monoxide on metals, M, is considered to be M + CO = M–CO. Thus, $H_{cc} = \{E(\text{M–M}) + E(\text{C–C})\}/2$; $H_{ii} = A_0 - I_M + W_e$, where $A_0$ is the electron affinity of carbon, and $I_M$ is the ionization potential of metals. *E*(C–C) was taken as 80.5 kcal. (*cf.* ref. *i*). [m] G. E. Moore and H. W. Allison, ref. 20. [n] I. Higuchi, T. Ree and H. Eyring, *cf.* Table III(B) in this paper. [p] J. K. Roberts, *Proc. Roy. Soc.* (*London*), **A152**, 445 (1935). [q] O. Beeck, "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., 1950, p. 151. [r] T. Kwan, footnote *q*, Vol. VI, 1955, p. 67. [s] L. Bagg and F. C. Tompkins, *cf.* ref. 35. [t] O. Beeck, *Disc. Faraday Soc.*, **8**, 118 (1950). [u] T. Kwan, *J. Research Inst. Catalysis*, Hokkaido Univ., **1**, 95 (1949). [v] D. D. Eley, *cf.* ref. 21. [w] R. T. Davis, Jr., THIS JOURNAL, **68**, 1395 (1946). [x] O. Beeck, W. A. Cole and A. Wheeler, *Disc. Faraday Soc.*, **8**, 314 (1950).

The bond eigenfunctions $\psi$ of multiple adsorption bonds, *e.g.*, M=O and M≡N, are considered as $\psi = C_c\psi_c(\text{M=O}) + C_i\psi_i(\text{M}^+\text{–O}^-)$ for M=O and $\psi = C_c\psi_c(\text{M≡N}) + C_i\psi_i(\text{M}^+\text{=N}^-)$ for M≡N. Here $\psi_c(\text{M=O})$ and $\psi_c(\text{M≡N})$ are the bond eigenfunctions of the covalent bonds in the corresponding adsorption bonds, and $\psi_i(\text{M}^+\text{–O}^-)$ and $\psi_i(\text{M}^+\text{=N}^-)$ are the ionic eigenfunctions of the bonds, the states of which are shown in the parentheses. The energies of the multiple adsorption bonds are then given by eq. 1. Here, $H_{cc} = \{2E(\text{M–M}) + D(O_2)\}/2$, and $H_{cc} = \{3E(\text{M–M}) + D(N_2)\}/2$ for the adsorption bonds, M=O and M≡N, respectively, $D(O_2)$ and $D(N_2)$ being the dissociation energies of $O_2$ and $N_2$. The energies, $H_{ii}$, are given by the following expressions; $H_{ii} = {}^1/_2\ \{2E(\text{M–M}) + D(O_2)\}/2 + A_0 - \text{I} + ({}^8/_9)\ (e^2/r_{MA})$ for the state, $\text{M}^+\text{–O}^-$; $H_{ii} = ({}^2/_3)\{3E(\text{M–M}) + D(N_2)\}/2 + A_0 - \text{I} + ({}^8/_9)\ (e^2/r_{MA})$ for $\text{M}^+\text{=N}^-$.

The agreement between the calculated and observed adsorption heats is generally good, except for the system, oxygen on nickel, where the observed heat is very much larger than the calculated one. The disagreement may be due to the oxidation of nickel which occurs with the chemisorption.

Eley[17] used the empirical formula, (6), in calculating the chemisorption heat $\Delta H_0$ for the system, hydrogen on W. This method has been extended to calculate the values of $\Delta H_0$ in other systems[21,26] with reasonable success. If we apply eq. 6 to the systems, Ba on W and Sr on W, the calculated adsorption heats for these systems are 4280 and 1772 kcal., respectively, whereas the observed values are 83 and 79 kcal.[20] Thus, the applicability of eq. 6 is limited to the cases where $\mu'$ is very small. As already mentioned, our theory has a quantum mechanical basis, and can treat all

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(26) B. M. W. Trapnell, "Chemisorption," Academic Press, Inc., New York, N. Y., 1955, p. 145.

kinds of adsorptions ranging from pure ionic to pure covalent.

**C. Calculations of $\delta(\Delta H)$.**—The conditions, $C\alpha\theta << 1$ and $U_i$ very small, do not hold for the systems, Ba on W and Sr on W, since in these cases the polarizabilities of the adatoms, $\alpha$, and the ionic character of the adsorption bonds are large. Thus, the decrease of the desorption heats, $\delta(\Delta H)$, with $\theta$ for the systems are calculated from eq. 14a. Moore and Allison[20] measured the rates of desorption of these systems at two or three different temperatures over a limited range. Thus it is impossible to calculate the activation heats accurately as a function of $\theta$ from their data. According to eq. 24a the activation heats are equal to the desorption heats. Detailed studies for the rates of desorption of the systems over a wide range of temperatures and coverages are highly necessary for the test of eq. 14a.

For the systems, hydrogen on metals and oxygen on metals, the decrease of the desorption heats with $\theta$, $\delta(\Delta H)$, is calculated from eq. 15b. Here, $\mu'$ is obtained from the contact potential, $V$, through the relation of 13, as previously mentioned. In the literature, the contact potentials for adsorption systems are more frequently measured at $\theta = 1$ than over the whole range of $\theta$.[14,24,27,28] The values of $\delta(\Delta H)$ are calculated from (15b) using $V_1$ and assuming the linearity relation of $V$ *vs.* $\theta$. The calculated values of $\delta(\Delta H)$ are shown by dotted lines in Fig. 4. Part A shows the relation of $\delta(\Delta H)$ *vs.* $\theta$ for the system, hydrogen on W. The experimental points are taken from Trapnell's curve,[29] which contains not only his own data, but also the data due to Roberts,[30] Beeck,[31] Wheeler,[32] and Frankenburg.[33] Straight lines (2) and (1) were drawn using the value of $V$ at $\theta = 1$ obtained by Mignolet[14,24] and Bosworth,[27] respectively. The former used the vibrating-condenser method while the latter employed the electron-emission method. We cannot decide which is right. In any case, one sees that the experimental points lie in between the two theoretical straight lines.

Part B represents the results obtained for the system, oxygen on W. The experimental points are due to Bosworth and Rideal.[34] The theoretical straight line is drawn using the contact potential at $\theta = 1$ found by Bosworth.[28] In Part C, are shown the results obtained for the system, hydrogen on Ni. The experimental points are reproduced from Beeck's paper,[31] and the theoretical line is drawn by making use of Mignolet's value[24] of $V$ at $\theta = 1$. The results for the system, hydrogen on Fe, are shown in Part D. The experimental points are calculated from the data of Bagg and Tompkins.[35] Here $\Delta H_0$ was taken as 31 kcal.,[35] which was obtained by extrapolating the adsorption heats at $\theta$ ranging from 0.2 to 0.4 to $\theta = 0$. Because of the lack of reliable contact potentials, we use $V = 0.39$ v. at $\theta = 1$ for the system hydrogen on Fe.[36] This value seems reasonable in view of the value $V_1 = 0.345$ v. for the system, hydrogen on Ni. The theoretical straight line was drawn using this assumed value of $V$. From Fig. 4, one sees that eq. 15b describes the relation of $\delta(\Delta H)$ *vs.* $\theta$ correctly, but not quantitatively. There is a tendency for the experimental points to deviate considerably from the theoretical straight line at $\theta = 0.5$. The maximum deviation is usually 5 to 20 kcal. For the study of the cause of these deviations, we need more detailed measurements of $V$ and $\delta(\Delta H)$ over the whole range of $\theta$.

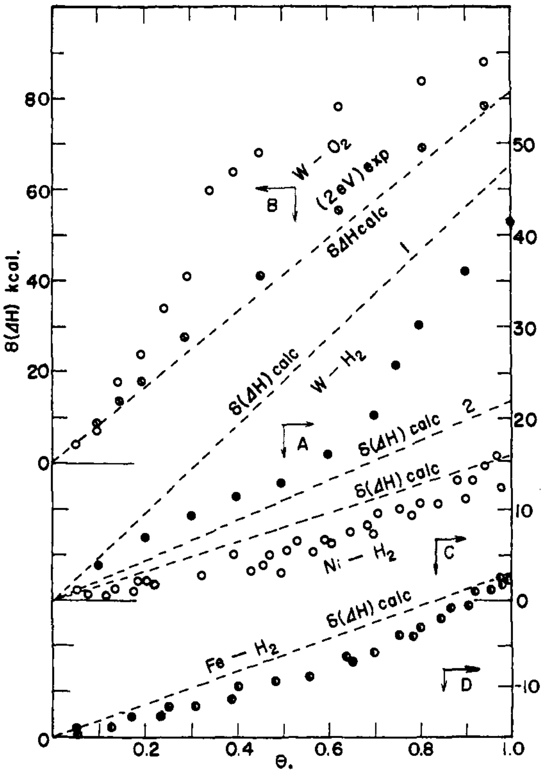

Fig. 4.—Decrease of desorption heat $\delta(\Delta H)$ *versus* coverage $\theta$. In this figure four examples, A, B, C and D, are shown. The coördinate used for each example is shown by arrows. The dashed straight lines are the theoretical values calculated from eq. 15b, using the values of $V_1$ and assuming the linearity of $V$ *versus* $\theta$. (A) The system hydrogen on W; two theoretical lines, 1 and 2, are drawn using two values of $V_1$ obtained by different authors.[14,27] (B) The system oxygen on W; the divided circles indicate the values of $\delta(\Delta H)$, which were calculated from (15b) by using the contact potentials $V$ measured at various values of $\theta$. (C) The system hydrogen on Ni. (D) The system hydrogen on Fe; the scale of the ordinate represents $\delta(\Delta H)$-15.

In the above, we have neglected the contribution of surface heterogeneity to $\delta(\Delta H)$, since it cannot be calculated theoretically. In some cases, "the heterogeneity contribution" may be very im-

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

(28) R. C. L. Bosworth, *J. Proc. Roy. Soc.*, *N.S.W.*, **79**, 166 (1945).

(29) B. M. W. Trapnell, *Proc. Roy. Soc.* (*London*), **A206**, 39 (1951).

(30) J. K. Roberts, *ibid.*, **A152**, 445, 477 (1935).

(31) O. Beeck, "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., 1950, p. 171.

(32) A. Wheeler's article in ref. 8, p. 439.

(33) W. G. Frankenburg, THIS JOURNAL, **66**, 1827 (1944).

(34) R. C. L. Bosworth and E. K. Rideal, *Physica*, **4**, 925 (1937).

(35) J. Bagg and F. C. Tompkins, *Trans. Faraday Soc.*, **51**, 1071 (1955). These authors claim that the adsorption heat rises sharply at $\theta < 0.05$ because of the heterogeneity of the surface they used. Thus, $\Delta H_0 = 36$ kcal. which they obtained, was not used here.

(36) According to Pauling's suggestion (ref. 12, p. 64), we estimate the electronegativity of iron as $X_{Fe} = 1.96$. Then $\mu'$ for the system H on Fe is 0.14, because $\mu' = X_H - X_{Fe} = 2.1 - 1.96$ (*cf.* ref. 12). Using this value of $\mu'$, $V_1$ is calculated as 0.39 v. from eq. 13.

portant. But it will be so only at small $\theta$. From Fig. 4, one sees that the agreement between theory and experiment at small $\theta$ is rather better than at $\theta = 0.5$. Thus the deviation is not due to the surface heterogeneity, but due to some other causes which are not clear at present.

**D. Calculations of Activation Free Energies.**—For determining the activation free energy for desorption, the logarithms of the logarithmic rates, $\ln(-\mathrm{d} \ln \theta/\mathrm{d}t)$, are plotted against $\theta$, as in paper I. The slope of the straight line thus obtained gives the constant $b$ in the Becker–Zeldovich eq. 20. Since $b$ is given by 22, $\delta(\Delta F_1^{\ddagger})$ is calculated from the experimental value of $b$. The intercept of the straight line with the ordinate allows the calculation of $\Delta F_0^{\ddagger}$ (*cf.* eq. 21).

**1. The Systems, Ba on W and Sr on W.**—We calculate the logarithmic rates from the curves of $\theta$ *vs.* $t$ (time) given by Moore and Allison.[20] The results are shown in Fig. 5. The straight lines are drawn using the least-mean-square method. The values of $b$, $\delta(\Delta F^{\ddagger})$ and $\Delta F_0^{\ddagger}$ were determined from the slopes of the straight lines and from the intercepts of the latter with the ordinate, and are summarized in Table IIIA. From $\Delta F_0^{\ddagger}$ at different temperatures, one obtains $\Delta H_0^{\ddagger}$ and $\Delta S_0^{\ddagger}$; the latter are tabulated in Table IIIB.

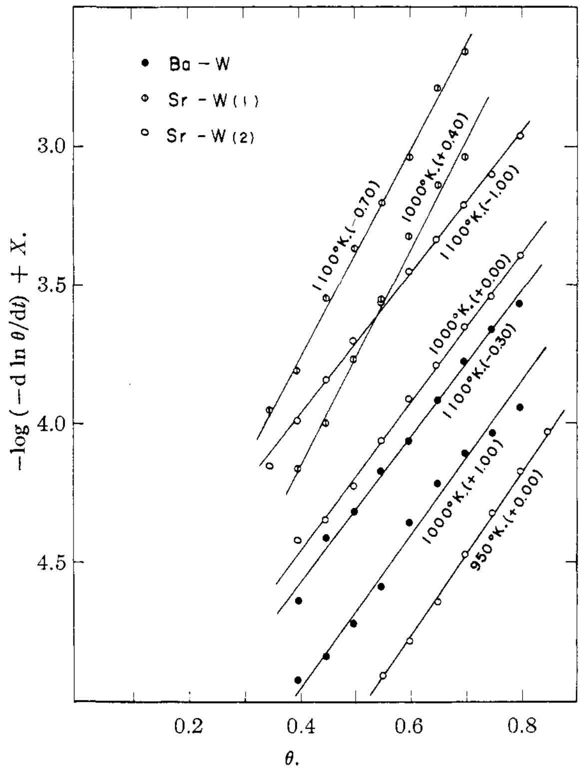

Fig. 5.—Logarithms of logarithmic desorption rates *versus* $\theta$ for the systems, Ba on W and Sr on W. In order to show all the data in a single figure, the values of $\log(-\mathrm{d} \ln \theta/\mathrm{d}t)$ are each displaced by an appropriate value $X$. This value of $X$ is the number in the parentheses on each straight line.

Since the ionic characters of the adsorption bonds, Ba–W and Sr–W, are large, we use 25a in calculating $\delta(\Delta F^{\ddagger})$ for these systems theoretically. The moment, $\mu'$, is determined from the curves of $V$ *vs.* $\theta$; $\sigma_m$, $d_1$ and $r_i$ are the structural constants depending on the desorption systems. We use $\sigma_m = 4.89 \times 10^{14}/\text{cm.}^2$,[20] $d_1 = 4.45$ Å.[20] $\theta_m$ is determined from the relation $C\alpha\theta_m = 0.013$, which is a negligible quantity compared to unity; $\theta_m = 0.0043$ for Ba on W, $\theta_m = 0.0081$ for Sr on W, where the $C\alpha$'s in Table I have been used. The values of $\mu'/2$ $(=\mu_0)$ and $r_i$ are given in Table I. The calculated $\delta(\Delta F_1^{\ddagger})$ and $b$ are compared with the observed quantities in Table IIIA and IIIB. The agreement is satisfactory.

TABLE IIIA[a]

| Temp., | Ba–W | | | Sr–W (1) | | | Sr–W (2) | | |
|---|---|---|---|---|---|---|---|---|---|
| °K. | $\Delta F_0^{\ddagger}$ | $b$ | $b_{\text{calcd.}}$ | $\Delta F_0^{\ddagger}$ | $b$ | $b_{\text{calcd.}}$ | $\Delta F_0^{\ddagger}$ | $b$ | $b_{\text{calcd.}}$ |
| 950 | .. | .. | .. | .. | .. | .. | 86.2 | 6.74 | 7.20 |
| 1000 | 93.6 | 6.56 | 6.59 | 89.1 | 9.12 | 6.84 | 86.2 | 6.12 | 6.84 |
| 1100 | 94.1 | 6.05 | 5.99 | 90.0 | 8.71 | 6.22 | 87.4 | 5.87 | 6.22 |

TABLE IIIB

| | $\delta(\Delta F_1^{\ddagger})_{\text{obsd.}}$, kcal. | $\delta(\Delta F_1^{\ddagger})_{\text{calcd.}}$, kcal. | $\Delta H_0^{\ddagger}$, kcal. | $\Delta S_0^{\ddagger}$, e.u. |
|---|---|---|---|---|
| Ba–W | 13.1 | 13.1[b] | 88.5 | − 5.1 |
| Sr–W (1) | 18.6 | 13.6[b] | 78.8 | −10.3 |
| Sr–W (2) | 12.5 | 13.6[b] | 78.4 | − 8.1 |

[a] All the values of $b_{\text{calcd.}}$ in this table were calculated from $b = \delta(\Delta F_1^{\ddagger})/RT$ by using the values of $\delta(\Delta F_1^{\ddagger})_{\text{calcd.}}$ in Table IIIB. [b] Calculated from eq. 25a. The necessary data for the calculations are shown in the text.

**2. The System Oxygen on W.**—The experimental points in Fig. 6 were obtained from the data of Bosworth and Rideal.[34] One sees that in this case, also, the Becker–Zeldovich equation holds satisfactorily. The parameters $b$, $\Delta F_0^{\ddagger}$ and $\delta(\Delta F_1^{\ddagger})$ are determined from Fig. 6, and tabulated in Table IV. It is interesting to note that $\delta(\Delta F_1)$ is independent of temperature. This fact indicates that 26 is correct, consequently that eq. 27 is true. Also we find the following interesting facts: (i) $\Delta F_0^{\ddagger}$ is about constant irrespective of temperature, *i.e.*, $\Delta S_0^{\ddagger} \approxeq 0$. (ii) The average value of $\delta(\Delta F_1^{\ddagger})$, 43.0 kcal., is nearly equal to the value, 41.0 kcal., calculated by 25b, where $V_1 = 1.78$.[28] This fact indicates that our theory is correct. From the fact $\delta(\Delta F_1^{\ddagger}) = \delta(\Delta H_1^{\ddagger}) = eV_1$, we can conclude that the rate-determining step is monomolecular. If it is bimolecular, the observed $\delta(\Delta F_1^{\ddagger})$ should be equal to $2eV_1$. Thus, our theory also provides a

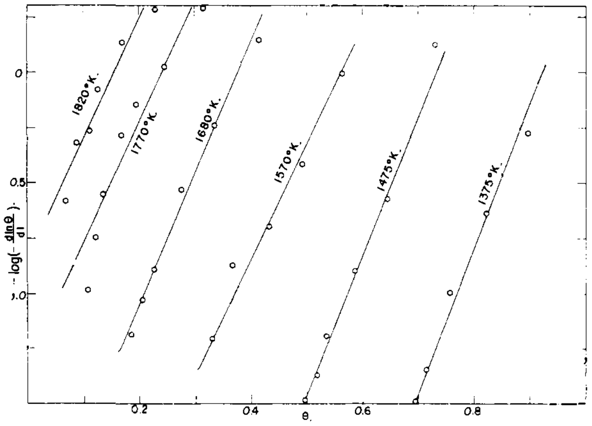

Fig. 6.—Logarithms of logarithmic desorption rates *versus* $\theta$ for the system oxygen on tungsten.

good tool for studying the mechanism of desorption and adsorption.

The small activation entropy found above, $\Delta S_0^{\ddagger} \simeq 0$, is explained as follows: let $S_0^{\ddagger}$ be the entropy of the activated state of a surface complex, MA, on a bare surface. $S_0^{\ddagger}$ is expressed by $S_0^{\ddagger} = S_0 - S_r + S_f$. Here $S_0$ is the entropy of the surface complex, MA. In the desorption, an electron making the bond M–A is transferred to M. The *recombination* of the electron with the atomic kernal of M accompanies the entropy decrease, $S_r$. Atom, A, increases its entropy by $S_f$, being *freed* somewhat from M. Thus, one obtains $\Delta S_0^{\ddagger} = S_0^{\ddagger} - S_0 = S_f - S_r$. It seems that $S_f \simeq S_r$, since $\Delta S_0^{\ddagger} \simeq 0$. Because of the latter condition, it is true that $\Delta F_0^{\ddagger} = \Delta H_0^{\ddagger} = \Delta H_0 = E$. Actually, the mean average value of $\Delta F_0^{\ddagger}$, 122 kcal., is approximately equal to the calculated bond energy $E$ of W:O, where $E$ = 116 kcal. (*cf.* Table II).

TABLE IV

DESORPTION DATA OF THE SYSTEM $O_2$ ON W

| $T$, °K. | $b_{\text{exp.}}$ | $\delta(\Delta F_1^{\ddagger})$ | $\Delta F_0^{\ddagger}$ | $b_{\text{calcd.}}$[a] |
|---|---|---|---|---|
| 1375 | 15.2 | 41.8 | 124 | 15.0 |
| 1475 | 14.4 | 42.2 | 122 | 13.9 |
| 1575 | 12.1 | 37.8 | 118 | 13.1 |
| 1680 | 13.8 | 46.1 | 127 | 12.2 |
| 1770 | 12.6 | 44.6 | 121 | 11.6 |
| 1820 | 12.6 | 45.7 | 120 | 11.3 |
|  | Av. | 43.0 | 122 |  |

[a] The $b_{\text{calcd.}}$ were calculated from $b = cV_t/RT$, where $V_t = 1.78$.[28]

## IV. Discussion

**A. Pure Covalent Adsorption.**—We showed that in pure covalent adsorption $C_i^2 = 0$ and $E = H_{cc}$ hold. Thus, in dissociative adsorption of homonuclear diatomic gases, the desorption heat, $\Delta H_0$, is given by the equation

$$\Delta H_0 = E(\text{M–M}) \tag{29}$$

The dissociative chemisorption of hydrogen on carbon may be considered as almost purely covalent. Thus, $\Delta H_0$ is given by $E$(C–C) = 58.6 kcal.,[12] which agrees reasonably well with the observed value, 50 kcal.[37]

On examining the data in Table II, one finds that eq. 29 holds approximately if $C_i^2$ is very small. Also one sees that the higher $E$(M–M), the larger is $\Delta H_0$. Thus, adsorbents with high vaporization heats adsorb more strongly than those with low vaporization heats. This fact is well known, and is often pointed out by many authors.[21,38] Our theory as formulated in eq. 1, predicts not only the above mentioned fact, but also that the desorption heat is larger, as the dissociation energy becomes higher. One may see this relation from the experimental desorption heats in Table II.

**B. Temperature Reducibility of Desorption Rates.**—Equation 20 may be integrated to give

$$\left(\frac{kT}{h}\, e^{-\Delta F_0^{\ddagger}/RT}\right) t = Ei\left(-\frac{\delta(\Delta F_1^{\ddagger})}{RT}\right) - Ei\left(-\frac{\delta(\Delta F_1^{\ddagger})\theta}{RT}\right) \tag{30}$$

Here

$$-Ei(-X) = \int_x^{\infty} \frac{e^{-\xi}}{\xi}\, \mathrm{d}\xi$$

*i.e.*, it is an exponential integral function; eq. 21 and 22 have been used in deriving 30.

Moore and Allison[20] showed that the rate curves for desorption, *i.e.*, $\theta$ *vs.* $t$, at two different temperatures are superposable when the time scale for the lower temperature is reduced by the appropriate factor. For example, the curve of $\theta$ *vs.* $t$ at 1000°K. for the Sr–W system is superposed on the curve at 1100°K. if the time scale of the former curve is multiplied by $^1/_{40}$. According to eq. 30,[39] the temperature reduction is possible only if $\delta(\Delta F_1^{\ddagger})/RT$ is independent of temperature. This condition holds when $\delta(\Delta H^{\ddagger}) = 0$ and $\delta(\Delta S^{\ddagger})$ is independent of temperature, because $\delta(\Delta F^{\ddagger}) = \delta(\Delta F_1^{\ddagger})\theta = \delta(\Delta H^{\ddagger}) - T\,\delta(\Delta S^{\ddagger})$. One naturally asks, is $\delta(\Delta F_1^{\ddagger})/RT$ independent of temperature or not? From Fig. 5, one sees that the slopes of the straight lines in the plots of log $(-\mathrm{d}\ln\theta/\mathrm{d}t)$ *vs.* $\theta$ are a function of temperature, *i.e.*, the lower the temperature, the steeper the slope (*cf.* the constants, $b$, in Table IIIA). Since the slope $b$ is given by $\delta(\Delta F_1^{\ddagger})/RT$, it is concluded that $\delta(\Delta H^{\ddagger}) \neq 0$.

Why then are the curves of $\theta$ *vs.* time, $t$, temperature reducible? We plotted the curves of $\theta$ *vs.* $t$ using the original data of Moore and Allison,[40] and tested the reducibility. We found that the temperature reduction is *apparently*, but not *exactly*, true. For example, in the system Sr on W, of which the reduced curve was represented by the corresponding curve in Fig. 9 in Moore and Allison's paper,[20] we found the following facts: in order to superpose exactly the curve of $\theta$ *vs.* $t$ at 1000°K. on the curve at 1100°K., the time scale of the former is multiplied by $^1/_{20}$ at $\theta = 0.9$, instead of the best over-all average factor $^1/_{40}$. In spite of this, the factor $^1/_{40}$ secures an apparently good reducibility as shown in their figure.[20] Because of the approximate nature of the temperature reducibility, we abandoned the use of the reduction factors for calculating $\Delta H_0^{\ddagger}$, and instead calculated $\Delta H_0^{\ddagger}$, $\Delta S_0^{\ddagger}$ and $\delta(\Delta F_1^{\ddagger})$ by the differential method already described.

**Acknowledgment.**—We wish to thank the California Research Corporation for the support of this work.

SALT LAKE CITY, UTAH

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(37) R. M. Barrer, *J. Chem. Soc.*, 1256 (1936).

(38) B. M. W. Trapnell, ref. 26, pp. 152–155.

(39) Moore and Allison[20] used eq. 30 to reproduce the experimental curves of $\theta$ *vs.* $t$ by assigning appropriate values to $\Delta F_0^{\ddagger}/RT$ and $\delta(\Delta F_1^{\ddagger})/RT$. They use for these parameters the symbols $\epsilon$ and $4V$, respectively.

(40) We thank Dr. Moore for sending the raw data used in constructing the temperature-reduced curves in the paper by Moore and Allison.[20]