The Ionic Adsorption of Gases on Semi-Conductors and Their Catalytic Activities

Part I. The Theory of Adsorption

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In the present paper a general theory of ionic adsorption of gases on semi-conductors is developed, with particular consideration for the combination of the types of semi-conductors and the signs of the electric charge on the adsorbed molecules. The results obtained agree qualitatively with experiments, but contradict predictions made by Dowden who in his theory does not take the space-charge layer near the surface into account. In the last section, physical models for adsorption sites are speculatively considered. A discussion of the catalytic activities of semi-conductors based on the present theory of adsorption is given. The applications to special reaction systems will be given in Part II of the present series.

With regard to the catalytic activities of semi-conductors Dowden[1] in his famous paper concluded that n-type (or p-type) semi-conductors are in general good catalysts for reactions associated with negative (or positive) ions. Experimental results, however, have shown that p-type semi-conductors are good catalysts for the decomposition of nitrous oxide[2,3] and for the oxidation of carbon monoxide[3], and that the adsorbed oxygen, an intermediate product in these reactions, which is adsorbed on p-type semi-conductors is negatively charged[4]. Now that Dowden's theory has been shown untenable, it is desirable to discuss the problem in all its aspects and to establish a new theory reconcilable with the empirical facts. The difficulty is that in a transient state quantities such as activation entropy and transmission probability along a reaction path can hardly be estimated, and it is therefore impossible at the present stage to perform a quantum-mechanical calculation of a rate constant. The alternative measure usually taken is to analyze the reaction mechanism by investigating the dependency of the reaction rate on temperature and partial pressure of the constituent gases. Sometimes, however, if experimental procedures are appropriately designed, it is possible to arrive straightforwardly at a proper understanding of catalytic processes by measuring the physical properties of the solid phase in stationary state.

Especially in the case of semi-conductor catalysts, the physical properties under working conditions are of great importance in the understanding of reaction processes, since these processes are seriously influenced by the gaseous environment. For instance, Wagner and Hauffe[5] have succeeded in determining the reaction mechanisms by measuring the electronic conductivity of the working semi-conductor catalysts, and the recent work of Sato[6] consisted in observing the rate of change in the colour of a $ZnO-ZnCr_2O_4$ catalyst used for the oxidation of carbon monoxide. These methods, however, cannot be applied to all reaction processes, since the required special properties may be difficult or impossible to measure. Thus it becomes advisable to develop a theory that involves only the common properties of the semi-conductor catalysts. One of common properties is the ionic adsorption of gases on catalysts. From this point of view, several authors[7] have advanced the theory of adsorption for semi-conductors, but they have not succeeded in formulating a general theory that gives a deep insight into the nature of catalytic activities. In view of these circumstances, the author has constructed a more general theory of adsorption

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[1] D. A. Dowden, J. Chem. Soc., Lond. **1950**, 242.

[2] K. Hauffe, R. Glang and H. J. Engell, Z. phys. Chem. **201**, 223 [1952]; G. Schmidt and N. Keller, Naturwiss. **37**, 43 [1950].

[3] G. M. Schwab and J. Block, Z. phys. Chem. N. F. **1**, 42 [1954]; cf. also the references cited in it.

[4] A. Kobayashi and S. Kawaji, unpublished data.

[5] C. Wagner and K. Hauffe, Z. Elektrochem. **44**, 172 [1938].

[6] T. Sato, Read at the 8th annual meeting of the Chem. Soc. Japan (1955).

[7] K. Hauffe and H. J. Engell, Z. Elektrochem. **56**, 366 [1952]; **57**, 763, 773 [1953]; P. Aigrain and C. Dugas, ibid. **56**, 363 [1952]; P. B. Weisz, J. Chem. Phys. **21**, 1531 [1953]; J. E. Germain, J. Chim. Phys. **51**, 691 [1954].

for semi-conductors, and discusses the common features of catalytic activities in these terms.

1. The Specific Nature of the Ionic Adsorption on Semi-Conductors

Recently Brattain and Bardeen[8] developed a method to determine the space-charge layer near the surface of a semi-conductor induced by ionic adsorption. Several authors[9] have applied this method to various systems and verified that space-charge layers are always induced by the adsorbate near the surface of a semi-conductor. The reason the ionic state of the adsorbate is stable remains, however, still unexplained even qualitatively. By way of example, let us take the case of the adsorption of oxygen on nickel oxide. The energy required to form from a molecule of oxygen two oxygen ions and two electrons on nickel oxide can be estimated as:

$$\begin{array}{lcr} 2\times(\text{work function of NiO}) & = & 2\times\ 4.8\ \text{eV} \\ -2\times(\text{electron affinity of atomic oxygen}) & = & -2\times\ 1.5\ \text{eV}\,[10] \\ +\ \ (\text{dissociation energy of } O_2) & = & 5.6\ \text{eV} \\ \hline \text{total energy} & & 12.2\ \text{eV}\,. \end{array}$$

In other words, the energy required is 6.1 eV per oxygen ion. The accepted value for the initial heat of adsorption, $\Delta H_{\text{ads}}(0)$, is, on the other hand, of the order of 1.2 eV. Hence, to obtain this value after compensation for -6.1 eV lost by the above-mentioned work, it is necessary to attribute the total energy, ca. 7.3 eV, to other sources, such as the Madelung energy, exchange energy, etc. Many of those energies can hardly be estimated either theoretically or experimentally at the present stage of knowledge, and so further discussion of the stability of the ionic states of adsorbates becomes hopeless. Be that as it may, it may well be asserted from the above estimation that in most cases of ionic adsorption on semi-conductors, the electron affinity or the ionization energy of the adsorbate and the work function of the adsorbent do not constitute a deciding factor in generating the heat of adsorption.

Another important feature of chemisorption which is observed in both metallic and semi-conductor adsorbents is the change in the heat of adsorption with coverage, Θ. With a few exceptions[11] an attribution of this change in the case of metallic adsorbents to an electric double layer at the surface of the adsorbent brings about wrong results[12]. In the case of semi-conductor adsorbents, however, such a double layer might play a principal role in the dependency of the heat of adsorption on the coverage, Θ, inasmuch as the surface double layer of semi-conductors is considerably thicker than that of metals and a small change in coverage may induce a large change in the work function. Thus one arrives at the situation that a statistical-mechanical theory of adsorption can be developed with due consideration for the relation between the space-charge layer and the change in the heat of adsorption with coverage.

2. The Formulation of Isotherm and Heat of Adsorption

It is assumed for simplicity that

> the crystal surface is an infinite plane represented by $x=0$ and that the electrostatic field is a function of only x and temperature, i.e., is independent of y and z, and that
>
> the heat of adsorption assumes the same value at each site, although the number of adsorption sites may change with coverage and temperature.

It may be further taken for granted without loss of generality in mathematical formulation that a negative charge is induced on the adsorbed particles.

Figs. 1(a) and 1(b) show respectively the band structure and the electrostatic potential near the surface of a semi-conductor with a negatively charged adsorbate. E_c and E_v indicate respectively the bottom of the conduction band and the top of the valence band of the semi-conductor. V_s and V_∞ indicate the values of the electrostatic potential at $x=0$ and at an infinite interior of the adsorbent, i.e., at $x=\infty$, respectively,

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[8] W. H. Brattain and J. Bardeen, Bell Syst. Tech. J. **32**, 1 [1953].

[9] A. Kobayashi and S. Kawaji, J. Phys. Soc. Japan **10**, 270 [1955]; S. Tanaka and M. Aoki, Japan. J. Appl. Phys. **22**, 311 [1953].

[10] L. M. Bramscomb and S. J. Smith, Phys. Rev. **98**, 1127 [1955].

[11] J. H. de Boer, Electron Emission and Adsorption Phenomena, 1935.

[12] R. Gomer, J. Chem. Phys. **21**, 1869 [1953].

and where $V_B = V_\infty - V_s$

is valid at all times.

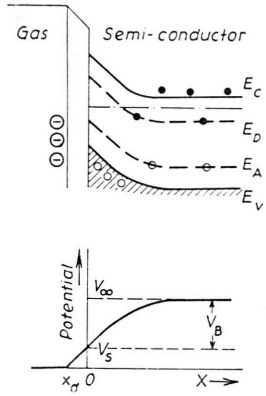

Fig. 1. (a) The band structure near the surface of a semi-conductor, with negatively charged adsorbate. (b) The electrostatic potential corresponding to Fig. 1(a).

The other symbols used in the present paper are tabulated as follows.

List of symbols

Subscripts:

- D: donor level in the interior of the semi-conductor
- A: acceptor level in the interior of the semi-conductor
- σ: adsorbed layer
- e: quasi-free electron in the semi-conductor
- h: positive hole in the semi-conductor
- $l1$ or $l2$: lattice site or interstitial site where an impurity level can be created

Quantities:

- N: number of electronic levels per cm³ or number of adsorption sites per cm²
- n: number of electronic levels occupied by an "electron" per cm³ or number of adsorbed particles per cm²
- $\Theta = n/N$: degree of occupation of a specified state
- a: partition function of an isolated particle in a specified state
- E: energy measured from the standard state in the case where there is no space charge
- ζ: FERMI level of the semi-conductor in the case where there is no space charge
- N_S: number of lattice points of cations or anions at surface per cm²
- $C_D = N_D/N_{l1}$, $C_A = N_A/N_{l2}$: concentration of impurity centers
- $C_\sigma = N_\sigma/N_S$: concentration of adsorption sites

At this point further assumptions are introduced with respect to the distribution of various electronic levels which might change with adsorption or temperature. Both donor and acceptor centers in the semi-conductor may exist simultaneously, but each type of impurity levels is only one sort.

The partition function for an adsorbed state inclusive of the solid phase, Q_{ads}, is given, according to the usual procedure [13], by

$$\begin{aligned}\ln Q_{\text{ads}} = \ln &\frac{N_S!}{n_\sigma!(N_S-N_\sigma)!\,(N_\sigma-n_\sigma)!} + n_\sigma \ln a_\sigma^* + (N_\sigma - n_\sigma)\ln a_\sigma \\ &+ \int \left[\ln \frac{N_{l1}!}{n_D!(N_{l1}-N_D)!\,(N_D-n_D)!} + \ln \frac{N_{l2}!}{n_A!(N_{l2}-N_A)!\,(N_A-n_A)!}\right]\cdot dx \\ &+ \int [(N_D - n_D)\ln a_D^+ + n_D \ln a_D + (N_A - n_A)\ln a_A + n_A \ln a_A^- \\ &\qquad + n_e \ln a_e - \ln(n_e!) + n_h \ln a_h - \ln(n_h!)]\cdot dx - W_{\text{int}}/kT\end{aligned}$$

where a_D^+ and a_A^- refer respectively to the ionized state of a donor level and the electron-trapped state of an acceptor level; a_D and a_A to the neutral states of the respective levels; and a_σ and a_σ^* refer respectively to a vacant adsorption site and an occupied one inclusive of the adsorbed particle. W_{int} is the mutual interaction energy between the particles consisting of adsorbates, electrons at various impurity levels, quasi-free electrons and positive holes.

Differentiation of $\ln Q_{\text{ads}}$ with respect to n_σ yields the chemical potential of adsorbed particles:

$$\begin{aligned}\frac{\mu_\sigma}{kT} = -\frac{\partial}{\partial n_\sigma}\ln Q_{\text{ads}} &= \ln\left(\frac{\Theta_\sigma}{1-\Theta_\sigma}\frac{a_\sigma}{a_\sigma^*}\right) + \frac{\partial N_\sigma}{\partial n_\sigma}\left[\ln(1-\Theta_\sigma) + \ln\frac{C_\sigma}{1-C_\sigma} - \ln a_\sigma\right] \\ &+ \int\left[\ln\left(\frac{\Theta_D}{1-\Theta_D}\frac{a_D^+}{a_D}\right)\cdot\frac{\partial n_D}{\partial n_\sigma} + \ln\left(\frac{\Theta_A}{1-\Theta_A}\frac{a_A}{a_A^-}\right)\cdot\frac{\partial n_A}{\partial n_\sigma} + \frac{\partial n_e}{\partial n_\sigma}\ln\left(\frac{n_e}{a_e}\right) + \frac{\partial n_h}{\partial n_\sigma}\ln\left(\frac{n_h}{a_h}\right)\right]\cdot dx \qquad (1) \\ &+ \int\left[\frac{\partial N_D}{\partial n_\sigma}\left\{\ln(1-\Theta_D) + \ln\frac{C_D}{1-C_D} - \ln a_D^+\right\} + \frac{\partial N_A}{\partial n_\sigma}\left\{\ln(1-\Theta_A) + \ln\frac{C_A}{1-C_A} - \ln a_A\right\}\right]\cdot dx + \frac{1}{kT}\frac{\partial}{\partial n_\sigma}W_{\text{int}}\,.\end{aligned}$$

This expression may be further simplified by the use of the condition for electrical neutrality:

$$n_\sigma + \int (n_{\mathrm{e}} + n_{\mathrm{A}})\,\mathrm{d}x = \int (n_{\mathrm{h}} + N_{\mathrm{D}} - n_{\mathrm{D}})\,\mathrm{d}x$$

and the condition for thermal equilibrium:

$$\frac{\Theta_{\mathrm{D}}}{1-\Theta_{\mathrm{D}}}\frac{a_{\mathrm{D}}^{+}}{a_{\mathrm{D}}} = \exp\left(\frac{\zeta - e\,V'}{k\,T}\right) = \frac{\Theta_{\mathrm{A}}}{1-\Theta_{\mathrm{A}}}\frac{a_{\mathrm{A}}}{a_{\mathrm{A}}^{-}} = \frac{n_{\mathrm{e}}}{a_{\mathrm{e}}}$$

and
$$\frac{n_{\mathrm{h}}}{a_{\mathrm{h}}} = \exp\left(\frac{-\zeta + e\,V'}{k\,T}\right)$$

where $V' = V_\infty - V$ and e is the elementary charge. Thus (1) comes out to be

$$\begin{aligned}\frac{\mu_\sigma}{k\,T} = \ln &\left\{\frac{\Theta_\sigma}{1-\Theta_\sigma}\frac{a_\sigma}{a_\sigma^{*}}\exp\left(\frac{-\zeta}{k\,T}\right)\right\}\\ &+ \frac{1}{k\,T}\left[\int V'\frac{\partial \varrho}{\partial n_\sigma}\,\mathrm{d}x + \frac{\partial}{\partial n_\sigma}W_{\mathrm{int}}\right]\\ &+ \frac{\partial N_\sigma}{\partial n_\sigma}\left[\ln(1-\Theta_\sigma) + \ln\frac{C_\sigma}{1-C_\sigma} - \ln a_\sigma\right]\\ &+ \int\left[\frac{\partial N_{\mathrm{D}}}{\partial n_\sigma}\left\{\ln(1-\Theta_{\mathrm{D}}) + \ln\frac{C_{\mathrm{D}}}{1-C_{\mathrm{D}}} - \ln a_{\mathrm{D}}\right\}\right.\\ &\qquad\left. + \frac{\partial N_{\mathrm{A}}}{\partial n_\sigma}\left\{\ln(1-\Theta_{\mathrm{A}}) + \ln\frac{C_{\mathrm{A}}}{1-C_{\mathrm{A}}} - \ln a_{\mathrm{A}}\right\}\right]\mathrm{d}x\,,\end{aligned}$$

in which ϱ denotes the space charge of the semi-conductor, and is defined by

$$\varrho = e\left[-n_{\mathrm{e}} + n_{\mathrm{h}} + (N_{\mathrm{D}} - n_{\mathrm{D}}) - n_{\mathrm{A}}\right]\,.$$

Here, W_{int} consists of the electrostatic energy $W_{\mathrm{e.s.}}$ and the short range interaction energy W_{short}. The term

$$\partial W_{\mathrm{e.s.}}/\partial n_\sigma + \int V'\cdot\partial\varrho/\partial n_\sigma\cdot\mathrm{d}x$$

may be expressed in a more compact form by the use of the Poisson equation:

$$\begin{aligned}\frac{\partial W_{\mathrm{e.s.}}}{\partial n_\sigma} &+ \int V'\frac{\partial\varrho}{\partial n_\sigma}\,\mathrm{d}x\\ &= \frac{1}{2}\frac{\partial}{\partial n_\sigma}\int_0^\infty \varrho\,V\,\mathrm{d}x + \int_0^\infty (V_\infty - V)\frac{\partial\varrho}{\partial n_\sigma}\,\mathrm{d}x\\ &= \frac{1}{8\,\pi}\left[V\frac{\partial^2 V}{\partial n_\sigma\,\partial x} - \frac{\partial V}{\partial x}\frac{\partial V}{\partial n_\sigma}\right]_{x=0}^{x=\infty} + e\,V_\infty\\ &= e\,V_\infty + \frac{1}{8\,\pi}\left[\frac{\partial V}{\partial x}\frac{\partial V}{\partial n_\sigma} - V\frac{\partial^2 V}{\partial n_\sigma\,\partial x}\right]_{x=0}\end{aligned}$$

where the second term in the right hand side is zero in so far as the electric field is continuous at $x=0$; hence this term may be equated to zero in the usual case.

Thus, one obtains the final expression for the chemical potential of the adsorbed particles:

$$\begin{aligned}\frac{\mu_\sigma}{k\,T} = \ln &\left[\frac{\Theta_\sigma}{1-\Theta_\sigma}\frac{a_\sigma\exp(-\zeta/k\,T)}{a_\sigma^{*}}\right] + \frac{e\,V_\infty}{k\,T} + \frac{1}{k\,T}\frac{\partial W_{\mathrm{short}}}{\partial n_\sigma}\\ &+ \frac{\partial N_\sigma}{\partial n_\sigma}\left[\ln(1-\Theta_\sigma) + \ln\frac{C_\sigma}{1-C_\sigma} - \ln a_\sigma\right] \qquad (2)\\ &+ \int\left[\frac{\partial N_{\mathrm{D}}}{\partial N_\sigma}\left\{\ln\Theta_{\mathrm{D}} + \ln\frac{C_{\mathrm{D}}}{1-C_{\mathrm{D}}} - \ln a_{\mathrm{D}}\right\}\right.\\ &\qquad\left. + \frac{\partial N_{\mathrm{A}}}{\partial n_\sigma}\ln(1-\Theta_{\mathrm{A}}) + \ln\frac{C_{\mathrm{A}}}{1-C_{\mathrm{A}}} - \ln a_{\mathrm{A}}\right\}\right]\mathrm{d}x\,.\end{aligned}$$

The last two terms in (2) which bear upon the migration of constituent ions of the semi-conductor will be called the electrolytic terms in the following discussion. They are of great importance from both a theoretical and an experimental standpoint, since in some adsorbate-adsorbent systems the adsorption is accompanied by a considerable amount of gaseous absorption which may have a serious effect upon the physical properties of the semi-conductor.

The chemical potential of the gaseous molecules, μ_{gas}, is given by [13]

$$\frac{\mu_{\mathrm{gas}}}{k\,T} = \ln P + \ln\left[\left(\frac{h^2}{2\,\pi\,m\,k\,T}\right)^{\frac{3}{2}}\frac{1}{k\,T}\frac{1}{j_{\mathrm{gas}}(T)}\right] \qquad (3)$$

where P and m denote respectively the partial pressure and the mass of the gaseous molecules concerned, and $j_{\mathrm{gas}}(T)$ is the partition function for the internal degrees of freedom of the molecules. In equilibrium with adsorption, $\mu_{\mathrm{gas}} = \mu_\sigma$ is valid, unless the adsorbed molecules are dissociated. Only molecular adsorption will be discussed here, since dissociative adsorption may be treated through the introduction of only a slight modification.

Equating (2) to (3), one obtains the adsorption isotherm [(E.T.) = (electrolytic terms)]:

$$\begin{aligned}\frac{P}{P_0} = \frac{\Theta}{1-\Theta}\exp&\left[\frac{e\,V_\infty}{k\,T} + \frac{1}{k\,T}\frac{\partial}{\partial n_\sigma}W_{\mathrm{short}} + (\mathrm{E.T.})\right]\\ = \quad&\frac{\partial N_\sigma}{\partial n_\sigma}\left[\ln(1-\Theta_\sigma) + \ln\frac{C_\sigma}{1-C_\sigma} - \ln a_\sigma\right]\\ &+ \int\frac{\partial N_{\mathrm{D}}}{\partial n_\sigma}\left[\ln\Theta_{\mathrm{D}} + \ln\frac{C_{\mathrm{D}}}{1-C_{\mathrm{D}}} - \ln a_{\mathrm{D}}\right]\mathrm{d}x \qquad (4)\\ &+ \int\frac{\partial N_{\mathrm{A}}}{\partial n_\sigma}\left[\ln(1-\Theta_{\mathrm{A}}) + \ln\frac{C_{\mathrm{A}}}{1-C_{\mathrm{A}}} - \ln a_{\mathrm{A}}\right]\mathrm{d}x\end{aligned}$$

where Θ is introduced in place of Θ_σ, according to the usual notation, and P_0 is defined as follows

$$P_0 = \frac{a_\sigma\exp(-\zeta/k\,T)}{a_\sigma^{*}}\cdot\frac{k\,T(2\,\pi\,m\,k\,T)^{3/2}}{h^3}\,j_{\mathrm{gas}}(T)\,.$$

The heat of adsorption can be obtained by aid of the Clapeyron equation, so that the isosteric heat of adsorption becomes

$$\begin{aligned}\Delta H_{\mathrm{ads}}(\Theta) &= k\,T^2\left(\frac{\partial\ln P}{\partial T}\right)_{n_\sigma} \qquad (5)\\ &= \Delta H_{\mathrm{ads}}(0) + k\,T^2\frac{\partial}{\partial\,T}\left[\frac{e\,V_\infty}{k\,T} + \frac{1}{k\,T}\frac{\partial W_{\mathrm{short}}}{\partial n_\sigma} + (\mathrm{E.T.})\right]\end{aligned}$$

where $\Delta H_{\mathrm{ads}}(0)$ is a contribution from the term of P_0, whose change with temperature is imperceptibly small and may be usually ignored.

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[13] R. H. Fowler and E. A. Guggenheim, Statistical Thermodynamics, 1939.

For further development it is necessary to obtain an explicit expression for V_∞ in (2). This proves feasible only for such special models as will be given in the following section.

3. Application to Special Models

(Case A)

At first one of the simplest cases is considered. A negative charge is induced on the particles adsorbed on an n-type semi-conductor with homogeneously distributed donor centers, where W_{short} and the migration of constituent ions may be neglected. The space-charge layer in this case may be approximately represented by SCHOTTKY's exhaustion layer[14], where the density of space charge ϱ has a constant value, $e N_{\mathrm{D}}$, for $0 \leqq x \leqq x_1$ and is zero for $x > x_1$; x_1 is the thickness of the exhaustion layer. The POISSON equation $\Delta V = -4\pi\varrho/\varepsilon$ can easily be solved for such a charge-distribution, the solution being given by

$$V = 0 \qquad \text{for} \quad x \leqq x_\sigma ,$$

$$V = V_{\mathrm{S}}(x_\sigma - x)/x_\sigma \qquad \text{for} \quad x_\sigma \leqq x \leqq 0 ,$$

$$V_{\mathrm{S}} = |x_\sigma|\, 4\pi e\, n_\sigma/\varepsilon_\sigma ,$$

$$V = -\frac{2\pi e}{\varepsilon} N_{\mathrm{D}}\, x^2 + \frac{4\pi e}{\varepsilon} N_{\mathrm{D}}\, x + V_{\mathrm{S}} \qquad \text{for } 0 \leqq x \leqq x_1 ,$$

and

$$V_\infty = \frac{2\pi e N_{\mathrm{D}}}{\varepsilon} x_1^2 + V_{\mathrm{S}} = \frac{2\pi e}{\varepsilon N_{\mathrm{D}}} n_\sigma^2 + \frac{4\pi e\, |x_\sigma|}{\varepsilon_\sigma} n_\sigma \qquad \text{for } x \geqq x_1 \tag{6}$$

where $x=0$ is the surface of the semi-conductor, $|x_\sigma|$ is the thickness of adsorption layer and ε_σ and ε are respectively the dielectric constants of the adsorption layer and the semi-conductor. In deriving the solution, the condition for electrical neutrality, $n_\sigma = N_{\mathrm{D}}\, x_1$, has been used.

Combining (4), (5) and (6), one obtains the adsorption isotherm

$$\frac{P}{P_0} = \frac{\Theta}{1-\Theta} \exp\left[\frac{2\pi e^2}{k T \varepsilon}\, \frac{N_\sigma^2}{N_{\mathrm{D}}}\, \Theta^2 + \frac{4\pi e^2\, |x_\sigma|}{k T \varepsilon_\sigma} N_\sigma\, \Theta\right] \tag{7}$$

and the heat of adsorption

$$\Delta H_{\mathrm{ads}}(\Theta) = \Delta H_{\mathrm{ads}}(0) - \frac{4\pi e\, |x_\sigma|}{\varepsilon_\sigma} n_\sigma - \frac{2\pi e^2}{\varepsilon N_{\mathrm{D}}} n_\sigma^2 . \tag{8}$$

These results are slightly different from those by HAUFFE and ENGELL[7], and by AIGRAIN and DUGAS[7]; the latter group ignored the factor $\frac{1}{2}$ in the expression for the electrostatic energy, and thus derived an incorrect formula.

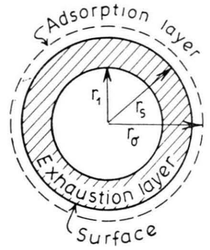

Fig. 2. Adsorption diagram for the case of spherical adsorbent.

In the case of an adsorbent of spherical form, slight modifications are introduced in (7) and (8): If r_{s} is the radius of the adsorbent, $r_{\mathrm{s}} - r_1$ the thickness of the exhaustion layer, and r_σ the distance between the center of adsorbent and the surface of adsorption layer (Fig. 2), the space-charge and the electrostatic field are given respectively by

$$\varrho = e N_{\mathrm{D}} \qquad \text{for} \quad r_{\mathrm{s}} \geqq r \geqq r_1 ,$$

$$\varrho = 0 \qquad \text{for} \quad r < r_1 ,$$

and

$$V = 0 \qquad \text{for} \quad r \geqq r_\sigma ,$$

$$V = \frac{4\pi e\, n_\sigma r_\sigma^2}{\varepsilon_\sigma}\left(\frac{1}{r} - \frac{1}{r_\sigma}\right) \qquad \text{for} \quad r_\sigma \geqq r \geqq r_{\mathrm{s}} ,$$

$$V = -\frac{2\pi e N_{\mathrm{D}}}{3\varepsilon} r^2 - \frac{c_1}{r} + c_2 \qquad \text{for} \quad r_{\mathrm{s}} \geqq r \leqq r_1$$

where c_1 and c_2 are defined by

$$c_1 = 4\pi e N_{\mathrm{D}}\, r_1^3/(3\varepsilon)$$

$$c_2 = \frac{2\pi e N_{\mathrm{D}}}{\varepsilon} r_{\mathrm{s}}^2 + \frac{4\pi e\, r_\sigma}{\varepsilon_\sigma}\left(\frac{r_\sigma}{r_{\mathrm{s}}} - 1 - \frac{r_\sigma}{r_{\mathrm{s}}}\,\frac{\varepsilon_\sigma}{\varepsilon}\right) n_\sigma .$$

In these equations r can be eliminated by utilizing the condition for electrical neutrality:

$$4\pi e\, n_\sigma r_\sigma^2 = (4\pi e N_{\mathrm{D}}/3)\ (r_{\mathrm{s}}^3 - r_1^3)$$

or

$$r_1^2 = [r_{\mathrm{s}}^3 - (3\, r_\sigma^2\, n_\sigma/N_{\mathrm{D}})]^{2/3} . \tag{9}$$

If the inequality $(3\, r_\sigma^2\, n_\sigma/N_{\mathrm{D}}\, r_{\mathrm{s}}^3) \ll 1$ is valid, (9) may be expanded in the form

$$r_1^2 = r_{\mathrm{s}}^2 - \frac{2\, r_\sigma^2}{N_{\mathrm{D}}\, r_{\mathrm{s}}} n_\sigma - \frac{r_\sigma^4}{N_{\mathrm{D}}^2\, r_{\mathrm{s}}^4} n_\sigma^2 - \frac{4\, r_\sigma^6}{3\, N_{\mathrm{D}}^3\, r_{\mathrm{s}}^7} n_\sigma^3 - \frac{7\, r_\sigma^8}{3\, N_{\mathrm{D}}^4\, r_{\mathrm{s}}^{10}} n_\sigma^4 - \dots . \tag{10}$$

The condition $(3\, r_\sigma^2\, n_\sigma/N_{\mathrm{D}}\, r_{\mathrm{s}}^3) \ll 1$ is fulfilled in the above-given example, since, provided $r_{\mathrm{s}} \simeq r_\sigma \sim 10^{-4}$ cm, $N_{\mathrm{D}} \sim 10^{19}$ cm^{-3} and $n_\sigma \sim 10^{14}$ cm^{-2}, one obtains

$$(3\, r_\sigma^2\, n_\sigma/N_{\mathrm{D}}\, r_{\mathrm{s}}^3) \simeq 0.3 .$$

By the use of (10) and the relation $r_\sigma - r_{\mathrm{s}} = |x_\sigma|$, one obtains

$$V_\infty = \frac{4\pi e\, |x_\sigma|}{\varepsilon_\sigma} n_\sigma \frac{r_\sigma}{r_{\mathrm{s}}} + \frac{2\pi e}{\varepsilon N_{\mathrm{D}}} n_\sigma^2 \frac{r_\sigma^4}{r_{\mathrm{s}}^4} + \frac{8\pi e}{3\varepsilon N_{\mathrm{D}}^2\, r_{\mathrm{s}}} n_\sigma^3 \frac{r_\sigma^6}{r_{\mathrm{s}}^6} + \frac{14\pi e}{3\varepsilon N_{\mathrm{D}}^3\, r_{\mathrm{s}}^2} n_\sigma^4 \frac{r_\sigma^8}{r_{\mathrm{s}}^8}$$

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[14] W. SCHOTTKY and E. SPENKE, Wiss. Veröff. Siemens-Werk. **18**, 1 [1939].

for the potential difference between $r=0$ and $r=r_\sigma$. As $r_\sigma/r_S \simeq 1$, the equation becomes

$$V_\infty = \frac{4\pi e\,|x_\sigma|}{\varepsilon_\sigma} n_\sigma + \frac{2\pi e}{\varepsilon N_D} n_\sigma^2 + \frac{8\pi e}{3\,\varepsilon N_D^2 r_S} n_\sigma^3 + \frac{14\pi e}{3\,\varepsilon N_D^3 r_S^2} n_\sigma^4 . \qquad (11)$$

By comparison equations (11) and (6) can be shown to be identical up to the second order terms. Since the terms of third and higher order in n_σ can be neglected; there is practically no difference between (11) and (6). The difference arising from these higher terms becomes appreciable only when the radius of the sphere and the concentration of donor levels are very small and the quantity of adsorbed molecules is considerably large.

The theory developed here can also be applied to the case in which a positive charge is induced on the particles adsorbed on a p-type semi-conductor, since then the change in sign of both the charge and the field gives rise to no change in the quantity $e V_\infty$.

(Case B)

Another simple but important case to be considered is the one in which a negative charge is induced on the particles adsorbed on an intrinsic semi-conductor, where W_{short} and the migration of constituent ions in the semi-conductor can be ignored. The space charge in this case is due to the polarization of quasi-free electrons and positive holes, both of which are assumed to obey the BOLTZMANN distribution law. Thus the space charge is given by

$$\varrho = e[n_{h\infty} \exp\{-e(V-V_\infty)/kT\} - n_{e\infty} \exp\{e(V-V_\infty)/kT\}]$$

where $n_{h\infty}$ and $n_{e\infty}$ are respectively the numbers of positive holes and quasi-free electrons per cm³ in the infinite interior of the semi-conductor.

This expression may be further simplified, by the relation $n_{h\infty} = n_{e\infty}$, to give:

$$\varrho = 2\,e\,n_{e\infty} \sinh\{e(V_\infty - V)/kT\} .$$

The corresponding POISSON equation is

$$\frac{\partial^2 V}{\partial x^2} = -\frac{4\pi\varrho}{\varepsilon} = -\frac{8\pi e n_{e\infty}}{\varepsilon} \sinh\frac{e(V_\infty - V)}{kT} .$$

This POISSON equation may be transformed into the simpler form,

$$\partial^2\Phi/\partial\xi^2 = \sinh\Phi \qquad (12)$$

by introducing the new variables

$$\Phi = e(V_\infty - V)/kT ,$$

and

$$\xi = \sqrt{8\pi e^2 n_{e\infty}/\varepsilon kT} \cdot x = x/L_D$$

where L_D is the DEBYE length.

Eq. (12) is the famous equation appearing in the theory of an electric double layer at an electrode surface, and has the solution [15]

$$\ln\tanh(\Phi/4) - \ln\tanh(\Phi_0/4) = -\xi$$

where Φ_0 is the value of Φ at $\xi = x = 0$. In the present problem, it is necessary to express Φ_0 as a function of n_σ. This can be performed by the use of the condition for electrical neutrality:

$$e\,n_\sigma = \int \varrho\,\mathrm{d}x = 2\,e\,n_{e\infty} \int_0^\infty \sinh\Phi \cdot L_D\,\mathrm{d}\xi ,$$

which, in conjunction with the relation

$$\partial\Phi/\partial\xi = -2\sinh(\Phi/2),$$

becomes

$$\frac{n_\sigma}{4\,n_{e\infty} L_D} = \frac{1}{2}\int_{\Phi_0}^{0} \frac{2\sinh(\Phi/2)\cdot\cosh(\Phi/2)}{-2\sinh(\Phi/2)}\,\mathrm{d}\Phi = \sinh\frac{\Phi_0}{2} ,$$

or

$$\Phi_0 = e V_B/kT = e(V_\infty - V_S)/kT \qquad (13)$$

$$= 2\ln\left[\frac{n_\sigma}{4\,n_{e\infty} L_D} + \left\{\left(\frac{n_\sigma}{4\,n_{e\infty} L_D}\right)^2 + 1\right\}^{1/2}\right].$$

On the other hand, V_S is given by

$$V_S = 4\pi e\,|x_\sigma|\,n_\sigma/\varepsilon_\sigma ,$$

so that the corresponding expressions for eV_∞/kT and $\partial\{eV_\infty/kT\}/\partial T$ are

$$\frac{eV_\infty}{kT} = \Phi_0 + \frac{eV_S}{kT} = \frac{4\pi e^2 |x_\sigma|}{kT\,\varepsilon_\sigma} n_\sigma + 2\ln\left[\frac{n_\sigma}{4\,n_{e\infty} L_D} + \left\{\left(\frac{n_\sigma}{4\,n_{e\infty} L_D}\right)^2 + 1\right\}^{1/2}\right], \qquad (14)$$

$$\frac{\partial}{\partial T}\left(\frac{eV_\infty}{kT}\right) = -\frac{4\pi e^2 |x_\sigma|}{kT^2\,\varepsilon_\sigma} - \frac{n_\sigma}{4\,n_{e\infty} L_D}\left[\left(\frac{n_\sigma}{4\,n_{e\infty} L_D}\right)^2 + 1\right]^{-1/2} \cdot \left[\frac{\partial \ln n_{e\infty}}{\partial T} + \frac{1}{T}\right]. \qquad (15)$$

Introduction of (14) into (4) yields the adsorption isotherm:

$$\frac{P}{P_0} = \frac{\Theta}{1-\Theta}[\lambda_1\Theta + \sqrt{\lambda_1^2\Theta^2 + 1}]^2 \cdot \exp\left(\frac{\lambda_2\Theta}{kT}\right), \qquad (16)$$

in which λ_1 and λ_2 are defined by

$$\lambda_1 = N_\sigma/(4\,n_{e\infty} L_D) \quad \text{and} \quad \lambda_2 = 4\pi e^2 |x_\sigma| N_\sigma/\varepsilon_\sigma$$

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[15] D. C. GRAHAME, Chem. Rev. **41**, 441 [1947].

where N_σ is the number of adsorption sites per cm². For the heat of adsorption, one obtains from (15), (5) and the relation $n_{e\infty} = \text{const} \cdot \exp(-\Delta E/2kT)$, the expression

$$\Delta H_{\text{ads}}(\Theta) = \Delta H_{\text{ads}}(0) - \lambda_2 \Theta - \lambda_1 \Theta [\lambda_1^2 \Theta^2 + 1]^{-1/2} \cdot [(\Delta E/2) + kT]\,, \tag{17}$$

where $\Delta E (= E_c - E_v)$ denotes the magnitude of the energy gap between the conduction and valence bands in the intrinsic semi-conductor.

In the above derivation of (16) and (17) it has been assumed that the quasi-free electrons and the positive holes obey the BOLTZMANN statistics, an assumption which is valid only when $\Delta E/2$ is large compared to kT and $e(V_\infty - V_S)$. When these conditions are not met one must apply the FERMI-DIRAC distribution function, and the resulting equations have no simple analytical solution. The order of magnitude of $e(V_\infty - V_S)$, on the assumption that $n_\sigma \sim 10^{14}/\text{cm}^2$, $n_{e\infty} \sim 10^{19}/\text{cm}^3$ and $L_D \sim 10^{-7}$ cm, is estimated by (13) to be

$$e(V_\infty - V_S) = kT\,\Phi_0 \simeq 2\,kT \ln 50 = 7.8\,kT\,.$$

Since in usual cases ΔE is larger than 1 eV, the BOLTZMANN statistics may be used as a good approximation.

Eq. (16) and (17), which have been derived for the intrinsic semi-conductor adsorbent, may also be used for the p-type semi-conductor adsorbent, provided $\Delta E_p/2$ $(= (E_A - E_v)/2)$ is large compared with $e(V_\infty - V_S)$ and kT, so that the BOLTZMANN statistics may be used as an approximation for the distribution of positive holes and of electrons trapped in acceptor levels. Here, one must be careful in assigning the correct value to ΔE_p, since the conductivities and HALL coefficients of powdered samples are influenced by several unfavourable factors [16]. In the study of catalysts, one of the appropriate methods of obtaining a correct value of ΔE_p may be the measurement of thermoelectric power at various temperatures [17].

It is to be remarked that in the Case B under consideration it is difficult to treat an adsorbent of spherical form, inasmuch as the fundamental differential equation for a strong electrolyte must be solved without recourse to the DEBYE-HÜCKEL approximation [18]. The analytical solution of this differential equation has not been obtained, so that a further discussion will not be given here.

For the same reason as given at the conclusion of the treatment of Case A, these above-obtained results can be applied, without alterations, to the case in which a positive charge is induced on the particles adsorbed on an n-type semi-conductor.

4. Comparison of the Theory with Experimental Results and Catalytic Activities of Semi-Conductors

It is not easy to secure reproducible data in the study of semi-conductor catalysts, since their physical properties are seriously affected by the history of the sample and the impurities contained in it. Hence only few experimental values of the heats of adsorption are available for comparison with the present theory. One set of such data is due to KINUYAMA [19], who studied the adsorption of carbon dioxide on zinc oxide catalyst at temperatures between 350° C and 500° C. From these isotherms one can obtain the isosteric heat of adsorption as shown in Fig. 3. It can been seen from this figure (Curve A) that the heat of adsorption rapidly decreases with increasing coverage — an increase of $3 \cdot 10^{13}$ molecules/cm² adsorbed corresponds to a decrease of 13 kcal/mole in ΔH_{ads} — and that the

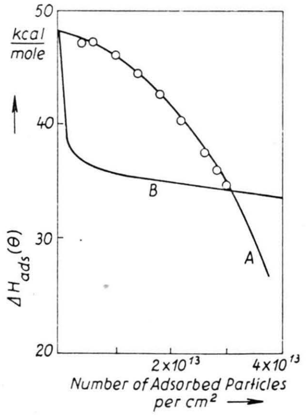

Fig. 3. The change in the heat of adsorption with coverage. Curve A is obtained from the isotherms for the adsorption of CO_2 on ZnO at 450° C and 500° C (by KINUYAMA).

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[16] H. K. HENISH, Z. phys. Chem. **198**, 41 [1951]; A. KOBAYASHI, Kagaku (Chemistry) **10**, No. 8, 22 [1955] in Japanese.

[17] A. KOBAYASHI, l. c. [16]; G. PARRAVANO, J. Chem. Phys. **23**, 5 [1955].

[18] R. A. ROBINSON and R. H. STOKES, Elektrolyte Solutions, Butterworth Sci. Publ., 1955.

[19] T. KWAN, T. KINUYAMA and Y. FUJITA, J. Res. Inst. Catalysis, Hokkaido Univ. **3**, 31 [1953].

decreasing curve can approximately be represented by a parabola:

$$\Delta H_{\mathrm{ads}}(\Theta) = 48 - 6.5 \cdot 10^{-14}\, n_\sigma - 1.3 \cdot 10^{-26}\, n_\sigma^2 \quad \text{(in kcal/mole)}. \qquad (18)$$

Such a rapid change in the heat of adsorption might be explained either by assuming the model of Case A given in the preceding section or by assuming some special distribution of active centers. Experimental evidence in favour of Case A indicating the existence of ionic adsorption could be demonstrated by an application of Brattain and Bardeen's method, but this has not yet been performed. Honig and Rosenbloom's test[20] was anticipated to choose between the two alternatives, but has been shown to lead to no tenable conclusion. On the assumption that the model of Case A is to be adopted the theoretical formula (8) can be compared with the empirical (18). If $|x_\sigma| \sim 10^{-8}$ cm and $\varepsilon \sim 5$, the numerical values of the physical constants ε_σ and N_{D} come out to be:

$$N_{\mathrm{D}} = 3.2 \cdot 10^{20}/\mathrm{cm}^3 \quad \text{and} \quad \varepsilon_\sigma = 6.4\,.$$

These are at least of the correct order of magnitude, since this N_{D}-value indicates that the concentration of impurities is 0.75 atom percent of the host crystal, and it is known that the negative ions have usually relatively large dielectric constants. Thus it may be considered as probable that the adsorbed molecules of carbon dioxide have a negative charge on the n-type semi-conductor ZnO.

The heat of adsorption as a function of coverage, Θ, in Case B is shown by the curve B in Fig. 3, in the construction of which it has been assumed that $\Delta E \simeq 1$ eV, the effective masses of quasi-free electrons and positive holes are nine times as large as that of free electrons, and the other physical constants are equal to those for curve A. The steep slope found in the initial stage of curve B may be smoothed out by an increase in the concentration of electronic carriers. Except in the region of very small Θ, the change of ΔH_{ads} with Θ is much slower in curve B than in curve A, and $\partial \Delta H_{\mathrm{ads}}/\partial n_\sigma$ becomes nearly constant at the final stage of curve B. This means that the potential drop V_∞ is due for the most part to V_{S}, and that the situation is similar to that in the case of ionic adsorption on metals, at least in so far as the electric double layer is concerned. Consequently, further quantitative discussion as to the change in heat of adsorption with coverage becomes impossible unless short-range interactions are taken into account. Be that as it may, it may be safely concluded that the decrease in heat of adsorption with increasing Θ is considerably small in Case B as compared with Case A.

Unfortunately experimental data are not available for direct comparison with the present theory for Case B, but the theory may be indirectly compared with the experimental results obtained by Brattain and Bardeen. They have measured the contact potential differences (C.P.) between platinum and germanium in various ambient gases at atmospheric pressure, and the changes in C.P. due to illumination, $(\Delta\,\mathrm{C.P.})_{\mathrm{L}}$. The result is that both (C.P.) and $(\Delta\,\mathrm{C.P.})_{\mathrm{L}}$ depend on the ambient gases and the time of contact of the crystal with the gases, or, in other words, on the kind and amount of adsorbate. The results are shown in Fig. 4, where $(\mathrm{C.P.})_0$ and $(\mathrm{C.P.})_0'$ are the values of (C.P.) for the case in which there is no space-charge layer near the surface of the germanium, i.e., the values of (C.P.) at $(\Delta\,\mathrm{C.P.})_{\mathrm{L}} = 0$. $(\Delta\,\mathrm{C.P.})_{\mathrm{L}}$ corresponds, according to the present notation, to the change in V_{B} with illumination, and therefore to a fraction of V_{B}. Though $(\Delta\,\mathrm{C.P.})_{\mathrm{L}}$ is not a simple function of V_{B} and furthermore depends on the intensity of illumination, there is a close parallel between $(\Delta\,\mathrm{C.P.})_{\mathrm{L}}$ and V_{B}.

$(\mathrm{C.P.}) - (\mathrm{C.P.})_0$ and $(\mathrm{C.P.}) - (\mathrm{C.P.})_0'$ also correspond to V_∞. The V_{B}-curves are schematically represented by the broken lines in Fig. 4 a.

On the other hand, the relation between V_{B} and V_∞ can be obtained by the use of (6), (13) and (14). The result obtained by assuming the values:

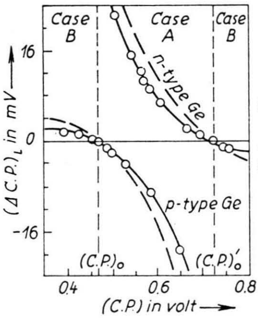

Fig. 4 a. The contact potential differences between Pt and Ge and their changes with illumination according to Brattain and Bardeen. The solid lines show experimental values and the broken lines are schematic representations of V_{B}.

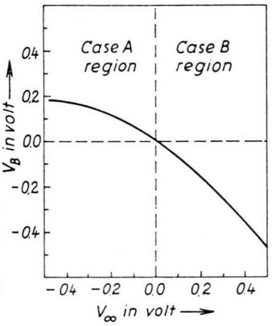

Fig. 4 b. Theoretical curve of V_{B} for a p-type adsorbent.

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[20] J. M. Honig and P. C. Rosenbloom, Canad. J. Chem. **33**, 193 [1955].

$$\varepsilon_\sigma = 5,\ \varepsilon = 5,\ N_A = 10^{18}/\text{cm}^3,\ \Delta E_p = 0.1\ \text{eV},\quad T = 300^\circ\ \text{K, and}\ |x_\sigma| = 10\ \text{Å}$$

is illustrated in Fig. 4 b. These values for the physical constants are of a reasonable order of magnitude in the usual semi-conductor catalysts but considerably different from those of Ge used in Fig. 4 a; nevertheless the general feature of the curves in Figs. 4 a and 4 b is the same. Now that the present theory of adsorption has proved to yield qualitatively correct results, this theory may well be assumed for the basis of further discussion of catalytic activities of semi-conductors.

Hedvall[21] has discovered an important effect of light on the adsorption of organic dyes on metallic sulphides. The amount of dye adsorbed on a pigment is increased by illumination with light of a wavelength lying within the fundamental absorption band of the solid, as shown in Fig. 5. Hedvall termed this effect "photoadsorption". Recently Kobayashi and Kawaji[9] found a similar effect for the adsorption of oxygen on ZnS, and observed at the same time a large change in contact potential.

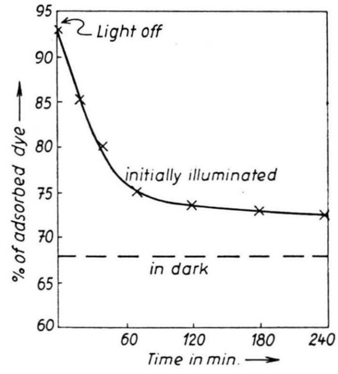

Fig. 5. Adsorption of lanasolgreen G (40 mg/l) on ZnS (Cu) in the dark and the effect of illumination by Hedvall[22].

The effect may be understood qualitatively by assuming the existence of a space-charge layer near the surface, as a decrease in the surface potential by irradiation brings about an increase in the heat of ionic adsorption. It is, therefore, quite natural to expect that in some cases the photo-excited adsorption seriously influences the reaction process in heterogeneous catalysis[23], but in order to discuss this effect quantitatively, a further development of the theory is required.

Adsorbents with strong adsorptive forces are not always good catalysts and in some cases may be rather inactive, since there may exist an optimum magnitude of adsorptive force for the adsorbent to be a good catalyst for a certain reaction. Particles adsorbed with such an optimum force may be in a reactive state, so that the adsorbent will act as an active catalyst under the condition that there are many reactive adsorbates. In a case such as Case A in which the heat of adsorption changes rapidly with coverage, only a limited number of adsorbed particles will participate in the reaction; in other words, the n-type semi-conductor is generally a less active catalyst than the p-type semi-conductor, if the amount of negatively charged adsorbates plays a decisive role in the rate of reaction concerned. The reverse is true with positively charged adsorbates. This theoretical conclusion accounts for the general feature of catalytic activities of semi-conductor catalysts, as mentioned in the beginning. The properties of ionic adsorption on semi-conductors are summarized in Table I, where (Dowden) and (Takaishi) have in mind a good catalyst as predicted by Dowden's and the present theory, respectively.

Type of semi-conductor	Thickness of the double layer in a semi-conductor: forming negative ions	Thickness of the double layer in a semi-conductor: forming positive ions	(E. A.) − (W. F.) in the case of the formation of negative ions	(W. F.) − (I. E.) in the case of the formation of positive ions
n-type	thick	thin (Takaishi)	large (Dowden)	small
p-type	thin (Takaishi)	thick	small	large (Dowden)

Table I. Properties of Ionic Adsorption on Semi-Conductors. (E. A.): electron affinity of the adsorbed particle, (I. E.): ionization energy of the adsorbed particle, (W. F.): work function of the semi-conductor adsorbent. (Dowden) and (Takaishi) have in mind a good catalyst as predicted by Dowden's and the present theory, respectively.

Other important facts are that in both Case A and B a change in the heat of adsorption with coverage is reduced by an increase in the concentration of electronic carriers, and that the change of Fermi-level with concentration of impurity levels is negligibly small under usual conditions, thus having little effect on the "equilibrium relation". In the first approximation, therefore, a semi-conductor may be con-

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[21] J. A. Hedvall, Handbuch d. Katalyse, Vol. VI, 1943, p. 578. Einführung in die Festkörperchemie, 1952.

[22] J. A. Hedvall, Z. phys. Chem. B **32**, 383 [1936].

[23] J. A. Hedvall, Z. anorg. allg. Chem. **239**, 713 [1938].

sidered a more active catalyst, the greater its electronic conductivity. In an extreme case, it may happen that catalytic activities of semi-conductors are controlled solely by the kind and concentration of impurity levels in the crystals. In such a case the activity is independent of the individual characteristics of the band structure. An example of such a case has been obtained by Kraus [24], who investigated the production of nitrous oxide by oxidation of ammonia on MnO-, CoO-, and NiO-catalysts. The results are shown in Fig. 6, and indicate that the catalytic activities of these oxides depend only on the concentration of excess oxygen, i.e., of impurity levels of the acceptor type. If factors other than the equilibrium amount of adsorption, such as the rate of transfer of electron or positive holes appreciably affect the catalytic activities of these oxides, one would not have been able to obtain such a simple relation as shown in Fig. 6, since the processes associated with electron transfer must be sensitively influenced by the individual nature of the crystal band structure. Kraus' result may belong to an exceptional case, nevertheless it is strong evidence for the importance of the space-charge layer in semi-conductor catalysts.

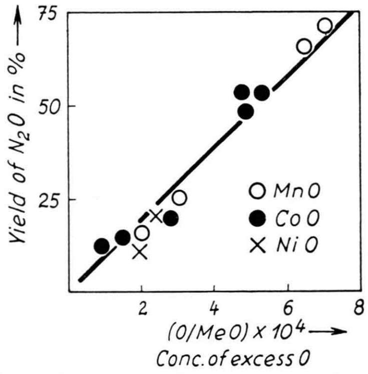

Fig. 6. Relation between catalytic activity and concentration of excess oxygen in MnO-, CoO- and NiO-catalysts for the oxidation of NH_3, at the ratio of $O_2/NH_3 = 1$ and at a reaction temperature of 300° C.

It is natural to expect that the catalytic activity of semi-conductors may be promoted by such impurities that they increase the electrical conductivity in accordance with the principle of controlled valency developed by Verway, Kröger and Hauffe [25]. Several authors [26] have investigated the catalytic activity of semi-conductors containing impurities from a viewpoint slightly different from that in the present theory; namely, on the assumption that the activities of the catalysts are determined by the rate of transfer of electrons or positive holes between adsorbent and adsorbate. This is in contrast to the present viewpoint that attaches a greater importance to the equilibrium amount of the adsorbed particles. Their results, however, have shown that the changes in the activation energy and in the entropy of reaction induced by doping the crystal with impurities were too complicated to be explained solely by the mechanism of electronic transfers. In these studies, the concentration of impurities was considerably higher in order of magnitude than in Kraus' case. Unfortunately such a high concentration of impurities introduces new complicated effects, such as the formation of large amounts of dislocation lines and phase separations. On the basis of the principle of controlled valency alone, it is impossible to continue the discussion of catalytic activities, since dislocation may play an important role in the formation of adsorption sites as will be considered in the next section, and moreover since the structure of the catalysts in question has not been fully examined in spite of the fact that a most careful treatment is required to obtain oxides homogeneously doped with impurities, as pointed out by Fensham [27].

5. The Adsorption Sites and Surface Trap Levels

In the preceding sections the question of the surface trap levels and the change of the number of adsorption sites has not been taken into consideration. The intrinsic nature of these factors remains still obscure, chiefly because of the difficulties involved in the experimental investigations, which were started only a few years ago. Some information, however, has been obtained and is very instructive in the study of semi-conductor catalysts.

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[24] W. Kraus, Z. Elektrochem. **53,** 320 [1949].

[25] E. J. W. Verwey et al., Philips Res. Rep. **5,** 173 [1950]; F. A. Kröger et al., Z. phys. Chem. **203,** 1 [1954]; K. Hauffe, Erg. exakt. Naturw. **25,** 193 [1951].

[26] C. Wagner, J. Chem. Phys. **18,** 69 [1950]; K. Hauffe, R. Glang and H. J. Engell, Z. phys. Chem. **201,** 223 [1952]; G. Parravano, J. Amer. Chem. Soc. **75,** 1452 [1953]; E. Molinari and G. Parravano, ibid. **75,** 5233 [1953]; G. M. Schwab and J. Block, Z. phys. Chem. N. F. **1,** 42 [1954]; K. Tarama, S. Teranishi and A. Yasui, Read at the 8th meeting of Chem. Soc. Japan, 1955.

[27] P. J. Fensham, J. Amer. Chem. Soc. **76,** 969 [1954].

The Madelung energy is one of the most important factors in the stability of the ionic state of adsorbed particles. For example, let us consider the Madelung energies at the sites [1] and [2] in Fig. 7. If the crystal has the structure of NaCl-type, the Madelung constants at [1] and [2] are 0.066 [28] and 0.874, respectively. This results in a difference of 9.76 eV in the Madelung energies of the ionic adsorbates at these sites on NiO whose lattice constant is 4.17 Å, a difference which is considerably large in comparison with the usual order of magnitude of initial heat of adsorption (2 eV). But such surface steps as shown in Fig. 7 may be extremely small in population owing to its special geometrical form, so that they may be of little importance in the study of the macroscopic properties of the crystals.

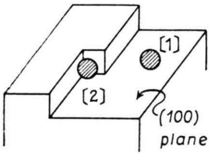

Fig. 7. The surface of a crystal and its adsorption sites.

On the other hand, a large number of surface steps may be formed by screw-dislocations, which at first would seem to be similar to those in Fig. 7 but actually are essentially different. Since the Madelung constants at the adsorption sites along screw-dislocation steps take the value intermediate between 0.066 and 0.874, it is possible that these sites may act as the so-called active centers for adsorption. If so, the adsorption sites may appear or disappear simultaneously with the screw-dislocations, the concentration of which is seriously affected by foreign ions and non-stoichiometry. This is one of the reasons why it is inadequate to discuss the catalytic activities of oxides doped with an impurity from the standpoint of the principle of controlled valency alone (see the preceding section).

Here it should be pointed out, however, that so far nothing definite is known about the concentration of dislocation steps on the surface of such small powdery crystals as catalysts, so that the present proposal is no more than a speculative consideration.

The surface trap levels in Si and Ge have been studied by several authors [29] in a vacuum of the order of 10^{-6} mm Hg. Recently Kobayashi and Kawaji [30] investigated the surface trap levels in ZnS at a high vacuum of 10^{-9} mm Hg and arrived at the conclusion that the surface trap levels of the donor type in ZnS result from anion vacancies concentrated near the surface. Surface trap level may then be treated in the same manner as acceptor and donor levels in the interior of a crystal.

6. Conclusion

One of the weak points of the existing theories of heterogeneous catalysis is that too much importance is attached to the kinematical expression of reaction processes with little consideration for the characteristics of the solids. As early as 1939 Wagner and Hauffe successfully interpreted the reaction processes in heterogeneous catalysis in terms of the specific properties of solids. But their ingeneous papers have not been properly appreciated, and no substantial progress has been made since. Recent developments in the study of semi-conductors have improved the situation so that the physical properties of semi-conductors can be used to help in the understanding of the catalytic process. Some of these important properties are the space-charge layer near the surface of a semi-conductor, the thermo-electric power and the electric resistivity at high frequency [31].

Since the principle of controlled valency is essentially concerned with the bulk properties of solids, and, on the other hand, the surface properties may be affected by a factor such as the concentration of screw-dislocations, catalytic activities cannot be discussed from the standpoint of controlled valency alone. It is true, however, that the application of valence-control to oxide catalysts will largely diminish the amount of absorbed gas, so that it will enable one to obtain stable catalysts and hence to separate "adsorption" from "absorption".

Although the present theory of adsorption is in accord with experimental results and explains the

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[28] K. F. Herzfeld, Z. phys. Chem. **105**, 329 [1923].

[29] W. H. Brattain and W. Shockley, Phys. Rev. **72**, 545 [1947]; W. H. Brattain, Phys. Rev. **72**, 345 [1947]; W. Shockley and G. L. Pearson, Phys. Rev. **74**, 232 [1948]; E. N. Clarke, Phys. Rev. **91**, 756 [1953]; **95**, 284 [1954].

[30] A. Kobayashi and S. Kawaji, J. Phys. Soc. Japan, in press.

[31] A. Kobayashi, l. c. [16]; E. J. W. Verwey, Semi-conducting Materials, 1952, p. 151.

general feature of the catalytic activity of semi-conductors, it yields no definite information as to the catalytic mechanism. It is anticipated, however, that through the introduction of the concept of a "virtual atmosphere", one will in time succeed in gaining a deeper insight into the catalytic mechanism at least in some cases. One of the best examples for such a case is found in the oxydation of carbon monoxide, as will be discussed in Part II of the present work.

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The Ionic Adsorption of Gases on Semi-Conductors and Their Catalytic Activities

Part II. The Law of the Virtual Atmosphere and Its Applications

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(Z. Naturforschg. **11 a**, 297—306 [1956]; eingegangen am 24. Januar 1956)

In Part I of the present work the theory of ionic adsorption was developed. In the present paper, the theory of the catalytic activity of semi-conductors is extended on the basis of the previous conclusions as to the ionic adsorption of gases. By introducing the concept of a "virtual atmosphere", a guiding principle for the selection of catalysts is obtained. The law of the virtual atmosphere here derived is applied to the oxidation of carbon monoxide on a semi-conductor, and provides the reasons the Rideal mechanism in this reaction is observed not on n-type but on p-type semi-conductor catalysts. Moreover, the relation between the catalytic activity and the history of a sample is reasonably interpreted in terms of the virtual atmosphere. Other reactions such as the decomposition of nitrous oxide and the synthesis of methanol are discussed qualitatively.

In Part I of the present work[1], the author developed a theory of ionic adsorption on semi-conductors with due regard to the space charge induced near the surface of a crystal, and discussed the catalytic activities of semi-conductors with special consideration for the types of semi-conductors and the signs of the electric charge on the adsorbed molecules. The results obtained, contradict the prediction made by Dowden[2] that p-type (or n-type) semi-conductors will in general be good catalysts for reactions in which the amount of negatively (or positively) charged adsorbates plays a decisive role in the rate of reaction concerned, and that the greater electronic conductivity, the more active the semi-conductor will be. In the previous theory the effect due to the migration of the constituent ions of a semi-conductor was not taken into consideration and the mechanism of catalytic reactions could not be discussed in detail.

It is now desirable, at least qualitatively, to take into account the migration of ions and the changes in the properties of a catalyst with the surrounding atmosphere. For this purpose it is convenient to introduce the concept of "the virtual atmosphere" which specifies the external conditions acting on the working catalyst.

1. The Law of the Virtual Atmosphere

The theory developed is based on the previous theory of adsorption in which the plane model of adsorption sites has been adopted for the sake of mathematical simplicity, but the essential results remain unaltered if the problem is treated from the standpoint of an active-center model; since the energy of the electric double layer which plays a primary role in the present theory is almost independent of the model of the adsorption sites.

If an n-type semi-conductor catalyst is placed in an oxidizing atmosphere, it will be gradually oxidized, approach a stoichiometric composition and consequently become less active owing to the decrease in the concentration of electronic carriers or in its ability for adsorption, as was shown in Part I. In the case of p-type semi-conductors, further oxidation brings about an increase of positive holes, and re-

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