

ADSORPTION ISOTHERMS OF NEUTRAL AND CHARGED PARTICLES  
ON SEMICONDUCTOR SURFACES

V. J. Lee

ABSTRACT

Theoretical gas adsorption isotherms of neutral and charged particles on semiconductor surfaces have been formulated, based on a mobile adsorption model. It is assumed that the temperature is moderately high so that the ad-particles can be ionized with or without dissociation. The derived adsorption isotherms are in conformity with experimental observations in the literature.

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## CHAPTER 5

### ADSORPTION ISOTHERMS OF NEUTRAL AND CHARGED PARTICLES ON SEMICONDUCTOR SURFACES

#### INTRODUCTION

Adsorption isotherms of neutral and charged particles express the equilibrium relationships between the gas phase and the adsorbed phase. . The development of these equilibrium relationships can be appreciated from two aspects.

First, it has been formulated in Chapters 3 and 4 that the variations of surface conductance and the thermionic work function are functions of the concentration of adions, which have also been identified as the slow surface states in Chapter 4. Other things being equal, the amount of these adions on a given semiconductor surface should be a function of its gas phase pressure at equilibrium conditions. Consequently, a correct adsorption isotherm for the adions should correlate the variation of the electronic properties of the semiconductor and the gas phase pressure. The development of an adion isotherm is a logical step in the study of gas-semiconductor surface interactions.

Second, adsorption of one or more than one of the gas reactants by a solid is a prerequisite for a chemical reaction which is catalyzed by the solid. Equilibrium relationships between the gas phase and the adsorbed phase or phases are necessary for the elucidation of the mechanism of the chemical reaction.

From the above two aspects, it is seen that the adsorption isotherms hold a key role for both the understanding of the effect of a gas on the electronic surface properties of a semiconductor and the catalytic action of the semiconductor on the chemical reaction between

gaseous species. It is with these appreciations that the author is motivated to write this chapter on the adsorption isotherms of neutral and charged particles.

Separate adsorption isotherms for each of the neutral and charged particles are formulated, and compared with experimental data in the literature. In the formulation of these isotherms the expressions previously derived in Chapter 2 for the surface potential,  $Y_s$ , are used together with other assumptions, which will be discussed in a later section after a brief literature survey.

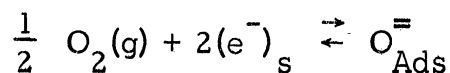
### LITERATURE SURVEY

Gas adsorption isotherms, resulting from either theoretical considerations or experimental observations before 1955 have been reviewed and redeveloped by Laidler<sup>(1)</sup> and by Trapnell.<sup>(2a)</sup> These adsorption isotherms relate the total amount of gas uptake by a specific surface area of a solid,  $\theta$ , and the gas phase pressure at equilibrium conditions. Naturally, the total amount of gas uptake,  $\theta$ , is the summation of all the various kinds of species in the adsorbed state. The equilibrium relationship between the gas phase pressure and the amount of one particular kind of species in the adsorbed state, say adions, is not known from the above-mentioned type of isotherms. In fact, the aforementioned isotherms recognize only one kind of specie in the adsorbed state, and this specie was assumed to be either molecules or atoms.

A later approach to the problem of gas adsorption was the recognition of the existence of adions with or without other species. The adions resulted from charge transfer between the adsorbed molecules or atoms (we shall define adsorbed particles or ad-particles to mean both adsorbed atoms and molecules) and the solid adsorbent, and marked the birth of the electron theory of heterogeneous catalysis. These concepts

which were proposed in 1938 are accredited to Wagner and Hauffe.<sup>(3)</sup> Subsequent investigators include Garner, S. Z. Roginsky, F. F. Volkenshtein, Engell and Hauffe, P. Aigrain and Dugas, P. B. Weisz, Dowden, Boudart, C. G. B. Garrett and others. For a review of these works, the reader is referred to Garrett<sup>(3)</sup> and Wolkenstein.<sup>(4)</sup> Since adsorption is the prerequisite for a catalytic chemical reaction as mentioned in the Introduction, the application of the idea of charge transfer to gas adsorption is a natural consequence. This latter aspect of gas adsorption has been investigated by Hauffe and Engell,<sup>(5)</sup> Aigrain and Dugas,<sup>(6)</sup> Weisz,<sup>(7)</sup> Takaishi,<sup>(8)</sup> Krusemeyer and Thomas,<sup>(9)</sup> Kogan<sup>(10)</sup> and Sandomirskii,<sup>(11)</sup> and Wolkenstein.<sup>(4)</sup> Some of these same authors have independently developed gas adsorption isotherms for adions or involving adions. We shall discuss these isotherms briefly.

Hauffe and Engell<sup>(5)</sup> have obtained adion isotherms by treating the adsorption process as a kind of quasi-chemical reaction at equilibrium condition. For example, they assume the reaction



which leads to the isotherm

$$[\text{O}^-]_{\text{Ads}} = (\text{constant}) n_s^2 (P_{\text{O}_2})^{1/2}$$

where  $n_s$  is the electron concentration at the surface region of an intrinsic semiconductor adsorbent. This isotherm was obtained by solving Poisson's equation in one dimensional form by assuming Boltzmann charge distribution in the space charge region;  $P_{\text{O}_2}$  is obviously the gas phase pressure of oxygen. Thus, essentially the adion isotherm is obtained by the application of the mass action law. This approach has been criticized by Kogan,<sup>(10)</sup> and Kogan and Sandomirskii<sup>(11)</sup> as "unclear" and "nonbasic."

Takaishi<sup>(8)</sup> has modified the above mass action law approach by assuming that the oxygen molecule is dissociated but only singly charged as  $[O^-]$  and that the adions are distributed randomly and independently on the sites of a crystal surface plane of an intrinsic semiconductor. For other assumptions Takaishi wrote: "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., 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." With this assumption Takaishi has applied Poisson's equation in one dimensional form to simplify his expressions. Then, he solved Poisson's equation in one dimensional form for both an assumed artificial charge distribution and a Boltzmann charge distribution in the space charge region of an intrinsic semiconductor. Takaishi then proceeded to derive a localized adion isotherm with an additional implied assumption that there exists on the crystal surface only one kind of ad-particles, namely, the adions.

An extension and a major advance of the above-mentioned approaches was made by Krusemeyer and Thomas.<sup>(9)</sup> These latter authors recognized that the neutral species may coexist with the charged particles and in equilibrium with them. They applied the Langmuir model of quasi-chemical reaction equilibrium to the neutral atoms only. For the equilibrium between the neutral atoms and the adions, Krusemeyer and Thomas applied the Fermi distribution function. By treating the surface atoms as donor or acceptor impurities, then they calculated the ratio of adions to adatoms by numerical methods for a surface which is free from fast surface states, although they included the fast surface states in the discussions. It goes without saying that Poisson's equation in one dimensional form is also used in their formulation for numerical

calculations. However, these authors used the Fermi charge distribution instead of the Boltzmann distribution used by previous authors for a more exact numerical evaluation.

The Russian workers have a different concept. Wolkenstein <sup>(4)</sup> assumed that one kind of atom can exist in a neutral state as well as in positively and negatively charged states. This means that a neutral particle can be a donor as well as an acceptor at the same time on a given solid surface. Using these same concepts Kogan <sup>(10)</sup> has obtained expressions for extremely low coverage of neutral and charged particles as a function of surface potential of a semiconductor. Kogan has made the following assumptions:

(a) "Each adsorption center may be filled independently by one of the three types of particles; neutral, negatively charged or positively charged.

(b) "The solid surface is energetically uniform, i. e., the solid surface has only one kind of adsorption center, whose number is assumed definite in a given system.

(c) "The energy of the system can be described as a summation of the energies of the separate adsorbed particles."

In a later article, Sandomirskii and Kogan <sup>(11)</sup> have applied the expressions for low surface coverage obtained by Kogan to formulate adsorption isotherms for the case of immobile, non-dissociative adsorption of molecules and molecular ions on semiconductors. The surface potential in Kogan's results was obtained by solving Poisson's equation in one dimensional form with a Boltzmann charge distribution. Their works were presented as pure theoretical hypotheses, without supporting data. None of their isotherms correspond to that of Engell and Hauffe, <sup>(5)</sup> and the latter were criticized.

From this brief survey, it is seen that, with the possible exception of the mass action approach, the aforementioned works on gas adsorption isotherms based on the charge transfer concept have the following points in common:

(1) Poisson's equation in one dimensional form has always been applied to obtain the surface potential  $Y_s$  for a few special cases. The surface potential is then used to formulate the adsorption isotherms. In connection with this, the solid surface has been also assumed to be energetically uniform by stating either that there is only one kind of adsorption center or that "the heat of adsorption assumes the same value at each site."

(2) The adsorbed particles are assumed to be localized (immobile) by either assuming the Langmuir adsorption model of quasi-chemical reaction or by stating that the surface has a definite number of fixed adsorption centers which can be filled independently.

#### A PROPOSED NEW GAS ADSORPTION MODEL

In this section, a new model of gas adsorption will be proposed. However, before we start on something new, it is appropriate to examine the old approaches to the problem. Undoubtedly there is a sound and stable foundation which has been laid down by previous workers as well as unstable scaffoldings which have to be removed for future buildings. To start this discussion, let us recall that the previous works on gas adsorption isotherms mentioned in the literature survey, have two points in common. We shall discuss both of them before the proposition of a new model for gas adsorption.

## On the Evaluation of Surface Potential, $Y_s$ , by

### Poisson's Equation in One-Dimensional Form

For the convenience of discussion, we shall redescribe briefly the definition of surface potential and the space coordinate system, which helps to define it.

Let us adopt the usual three dimensional orthogonal  $x, y, z$  coordinate system. The crystal surface of a semiconductor with infinite extent is represented by the  $y$ - $z$  plane at  $x = 0$ . The positive side of the plane,  $x = 0$ , is the gas phase; the negative side of the plane is the interior of the semiconductor of semi-infinite thickness.

Now let us imagine that there are adsorbed ions (adions), on the plane,  $x = 0$ , and an electrostatic field will be created in the interior underneath the surface. The electrostatic potential and the diffusion potential are related by

$$Y = qV \quad (5.1)$$

where  $q$  is the absolute electron charge. Poisson's equation can be written as

$$\nabla^2 V = -4\pi \rho q / \epsilon \quad (5.2)$$

where  $\nabla^2$  is the Laplacian operator, and  $\rho$  is the concentration of positively charged particles.

The surface potential is the diffusion potential at  $x = 0$ , namely,

$$Y_s = Y(0) = qV(0) \quad (5.1a)$$

In the previously mentioned works on adsorption isotherms based on "charge transfer adsorption," Poisson's equation in one dimensional form has been used, namely, in the  $x$ -direction only. The adions are considered either explicitly or tacitly on the plane,  $x = 0$ . The one-dimensional form of Poisson's equation may be written in the following equivalent forms



$$\frac{d^2V}{dx^2} = -4\pi \rho_q / \epsilon \quad (5.3a)$$

$$\frac{d^2Y}{dx^2} = -4\pi \rho_q^2 / \epsilon \quad (5.3b)$$

or

$$\frac{d^2u}{dx^2} = - \frac{4\pi \rho_q^2}{\epsilon kT} \quad (5.3c)$$

where

$$u(x) = Y(x)/kT \quad (5.3d)$$

Having introduced the definitions, we shall discuss  $Y(x)$  as defined in Equation (5.3b). As was pointed out in Chapter 2,  $Y(x)$  represents the space-and-time average of the electrostatic potential energy at a point  $x$  from the plane,  $x = 0$ , inside the space charge region of a semiconductor. Mathematically,  $Y(x)$  can be defined by the following expression,

$$Y(x) = \int_0^{\Delta t} \iint_{(S)} Y_1(t, x, y, z) dzdydt / \Delta t \quad \iint_{(S)} dzdy \quad (5.4)$$

where  $Y_1(t, x, y, z)$  is the instantaneous local diffusion potential in the

space charge region;  $\iint_{(S)} dzdy$ , denotes that the domain of integration

is over the entire  $y$ - $z$  plane at  $x$ ;  $\Delta t$  is the time interval of observation, which is assumed larger than or equal to the time of relaxation of the adsorbed species. The reason that  $Y(x)$  is taken as space-time average on the  $y$ - $z$  plane at  $x$  is because of the following considerations:

I. The free electrons and free holes in the space charge region are not localized. There is only a statistical macroscopic space-time average at a plane  $x = x$ . To understand this, a knowledge of what the electrons are doing in the semiconductor is necessary.

The motion of a free electron in a semiconductor is "similar" to the motion of a molecule in a gas phase. It performs random motion due to collisions, with or without an electric field. A mean free path and a mean free time between collisions are usually used to characterize the random motion of the free electrons<sup>(12a)</sup> in a semiconductor. It goes without saying that a free hole will behave the same way as a free electron. The free electrons are not localized, but cross the plane,  $x = x$ , in either direction randomly. In the language familiar to the chemist, Wolkenstein<sup>(4)</sup> wrote:

"The treatment of free electrons and free holes as free valencies is very convenient in describing chemical processes on the surface of a semiconductor. The following properties must be attributed to the free valencies (electrons or holes) of the catalyst in such a treatment.

(a) "Every free valence has a mean life time, that is, the free valencies can appear and disappear. A crystal continually produces and absorbs free valencies.

(b) "The free valencies are not localized in the lattice but migrate through the crystal. In other words, as long as we are dealing with an ideal lattice there is an equal probability of finding a free valence at any point of the crystal.

(c) "The equilibrium concentration of free valencies in the crystal and on its surface depends not only on the nature of the crystal, but also on external conditions: it increases with a rise in temperature and may be artificially increased or decreased under the influence of external agents (illumination, impurities, etc.).

(d) "There is a continuous interchange of valencies between the bulk and the surface of the crystal. Valencies pass from the surface into the bulk, and vice versa, so that the bulk of the crystal is like a reservoir, absorbing the free valencies of the surface and supplying them back to the surface....."

II. The adions on the plane,  $x = 0$ , may either vibrate over a highly restricted area in case of localized adsorption or migrate over an extended surface area in case of mobile adsorption. The local surface potential,  $Y_{\ell, s}$  and the diffusion potential  $Y_{\ell}(x)$  may vary with time in a random manner.

III. In an adsorption-desorption equilibrium, adions are added to or removed from the surface,  $x = 0$ , at any moment. The interchange may not occur at the same time and at the same point on the surface.

From these considerations of physical realities, it is obvious that any attempt to find the instantaneous local diffusion potential is both impractical and hopelessly impossible! It is an attempt to investigate statistical phenomena by classical mechanics. Granting that a general solution of  $Y_{\ell}(t, x, y, z)$  "can" be obtained, the determination of the initial condition will be another impossible task. The instantaneous charge distribution on the plane,  $x = 0$ , is independent of its initial condition.

In view of these considerations, the application of Poisson's equation to obtain  $Y(x)$  as the macroscopic space-time average is a very practical approach.

### Statistical Space-Time Average Coverage

Having discussed the surface potential,  $Y_s$ , obtained from the solution of Poisson's equation in one dimensional form as the statistical space-time average, the space-time-average concept can be used to obtain  $Y_s$  for low adion coverage. To do this, let us imagine that the dynamic statistical average coverage of adions on the semiconductor surface plane,  $x = 0$ , is so low that the adions and their respective images, as shown in Figure 5.1 can be considered as surface dipoles. This implies that each adion is associated with its respective image of opposite charge in the semiconductor.

Due to the adsorption-desorption equilibrium of the adions, and other motions of the adions as discussed previously, the distribution of the image dipoles on the semiconductor surface fluctuates frequently. For the convenience of illustrating the space-time-average concept, let us imagine that a macroscopic area  $S_A$  on the plane,  $x = 0$ , is divided into "n" sub-areas so that each sub-area is the minimum area required to accommodate one adion, e. g., a square surface lattice. Under conditions of low surface coverage the number of adions is much smaller than the number of sub-areas. Let us imagine further that on top of each sub-area there is a magic device, which can turn a light on when an adion is in the sub-area, and turn the light off when the adion is desorbed or moves away. Now the space-time average of adion coverage, say  $[D^+]$ , can be written as

$$[D^+] = \frac{\sum_{i=1}^n (\Delta t)_{i \text{ on}}}{(\Delta t)_{\text{ob}} S_A} \quad (5.5)$$

where  $(\Delta t)_{i \text{ on}}$  is the total time when the light is on at the sub-area,  $i$ , during the observation time  $(\Delta t)_{\text{ob}}$ , which is equal for every sub-area.

#### Low Surface Charge

When  $[D^+]$  is small so that each adion is associated with its image, the surface potential  $Y_s$  can be written using dipole theory as

$$Y_s \approx \frac{4\pi q^2 [D^+]}{\epsilon} r_o \quad (5.6)$$

where  $r_o$  is the average image dipole distance.

That is, for the low adion coverage the surface potential is proportional to the adion coverage. Now we shall ask: "Does the one dimensional form of Poisson's equation, Equation (5.3b), give this approximate relation for low adion coverage?"

The answer is "yes." Equations (2.20), (2.36), (2.46) of Chapter 2, give this approximate relation for low adion coverage. It is interesting to compare Equation (5.6) with any of the above-mentioned equations from Chapter 2, say Equation (2.36). Equation (2.36) can be written as

$$Y_s = kT u_s \cong kT(L_m/n_B)^{1/2} [D^+] < kT \quad (5.6a)$$

By combining Equations (5.6) and (5.6a) and recall that

$$L_m = 2\pi q^2/\epsilon kT$$

the resulting combination can be solved for the imagine dipole-layer spacing  $r_o$ . The result is

$$r_o = \frac{1}{2} (L_m n_B)^{-1/2} \quad (5.7)$$

Recall that the right hand side of Equation (5.7) is simply the screening length, or Debye length,  $L_s$ . Therefore

$$r_o = L_s \quad (5.7a)$$

Substitution of Equation (5.7a) into Equation (5.6) gives

$$Y_s = 4\pi q^2 [D^+] (L_s/\epsilon) < kT \quad (5.6b)$$

Similarly if acceptor adions are on the surface

$$Y_s = 4\pi q^2 [A^-] (L_s/\epsilon) < kT \quad (5.6c)$$

An expression equivalent to Equations (5.6b) and (5.6c) has been obtained previously by Morgulis,<sup>(13)</sup> who has also commented that "These ions build up here a double layer, . . . this double layer looks as if it were constructed of dipoles with a very large arm of the order of magnitude  $L_s/\epsilon$ ."

In view of the image dipole layer approximations which were used to obtain Equation (5.6) and the Equations (2.20), (2.36) and (2.46), it is concluded that the surface potential,  $Y_s$ , as obtained from the solution

of the one-dimensional Poisson's equation includes the limiting case of very low adion coverage, as long as a space-time statistical average of adion coverage, e. g.,  $[D^+]$ , exists as having been defined in Equation (5.5).

There is one additional assumption that the crystal surface at  $x = 0$  is energetically uniform so that there is no preferential statistical pattern of charge distribution on the surface. It is in this aspect that the above discussed approach may require additional refinement, such as dividing the crystal surface into various energy patches. However, such refinement would have to be constructed on the above discussed simple and fundamental approach. Furthermore, before this simple and fundamental approach is fully developed and checked against experimental observations, any refinement is too early and too subjective.

For experimental evidence, the approach of obtaining  $Y(x)$  by solving Poisson's equation in one dimensional form has been borne out by experimental observations on the variations of surface conductance,  $\Delta\sigma_s$ , and of thermionic work function  $\Delta\Phi_{th}$  of semiconductor surfaces due to gas adsorption, which have been presented in Chapters 3 and 4. Other quantitative correlations which utilize the discussed approach has been recently discussed and analyzed by Garrett<sup>(3)</sup> and by Wolkenstein.<sup>(4)</sup> Consequently, it is concluded that the evaluation of surface potential,  $Y_s$ , by solving the one-dimensional Poisson equation, (5.3b), is a sound and practical approach, at least at the present state of knowledge on the gas-semiconductor-surface interaction in general and gas adsorption on semiconductor surface in particular.

#### On the Hypothesis of Localized Adsorption

From the literature survey, it was seen that with the exception of the mass action approach, which is unclear, all other works on adsorption isotherms have assumed that the adsorbed species, both neutral and

charged particles, are localized. A survey of the literature shows that there is more to invalidate this hypothesis than we usually thought.

In his book, "The Dynamical Character of Adsorption," de Boer<sup>(14)</sup> has reviewed the evidences that the energy of activation for surface migration for both Van der Waal's adsorption and chemisorption is always smaller than the energy of adsorption or desorption. From the evidence, de Boer concluded that "As long as there is a dynamic equilibrium between adsorbed molecules and a gas involving numerous molecules adsorbing and desorbing every moment, there must be an equally active movement along the surface. We cannot expect the molecules to establish a dynamic equilibrium with the gas, involving a great probability of any individual adsorbed molecules escaping from the surface without there being an even greater probability of the same molecules moving along the surface."

De Boer's conclusion can be made more obvious from Figure 5.3, where  $w_j$  is the heat of adsorption or desorption,  $\Phi_j^0$  is the energy of activation for surface migration, and  $\Phi_j(y, z)$  is the restricting potential energy function on a crystal surface, (assumed to be square lattice in the schematic diagram).

Trapnell<sup>(2b)</sup> has also pointed out that "the surface bond breaks in desorption, but is only weakened during migration, and consequently the energy level from which migration is possible lies below that from which desorption is possible, . . . For this reason reversibly adsorbed layers tend to be mobile."

The distinction between localized particles and mobile particles on the surface has also been considered by Hill.<sup>(18)</sup> His theory indicates that the localized-mobile transition occurs at a temperature,  $T = \Phi^0/10 k$ , where  $\Phi^0$  is the energy barrier of a two dimensional potential energy function restricting the free translation of an ad-particle, and  $k$  is the Boltzmann's constant. That is, the restricting potential energy function can be written,

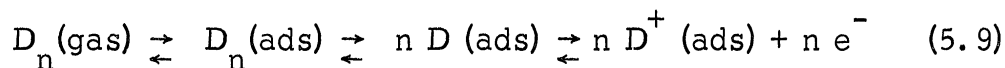
$$\phi(y, z) = (\phi^0/2) \left[ 2 - \cos \frac{2\pi y}{a} - \cos \frac{2\pi z}{a} \right] \quad (5.8)$$

where "a" is the distance between potential minima for a square surface lattice. Hill's result can be used as a criterion to determine whether an adsorbed layer is mobile, if it is confirmed by observation. This will be considered at the end of this section.

Studying the adsorption isotherm, we are concerned with adsorption-desorption equilibrium. Naturally, our attention is confined to the reversibly adsorbed particles which may include molecules, atoms and ions. However, only molecules are usually desorbed into the gas phase, but the adsorbed species may include atoms and ions in addition to molecules. Does this imply an exception to the rule that the reversibly adsorbed particles tend to be mobile? To clarify this point we shall consider the following general case of adsorption-desorption equilibrium involving adsorbed molecules, which can dissociate in the adsorbed state into adatoms. The adsorbed atoms, acting as donor or acceptor centers on a semiconductor surface, are in equilibrium with their ions and the charge carriers in the solid as assumed by Krusemeyer and Thomas<sup>(9)</sup> and others.<sup>(3, 4, 11)</sup> For convenience of representation, we shall discuss a donor molecule,  $D_n$  and the case of an acceptor molecule,  $A_n$ , should follow by analogy.

### Mobility of Adsorbed Particles

Now let us consider the following adsorption-desorption equilibrium:

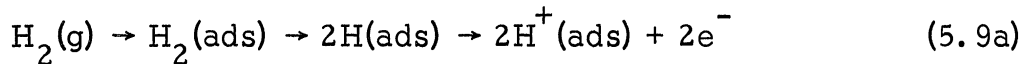


There are three different kinds of ad-particles, namely  $D_n(\text{ads})$ ,  $D(\text{ads})$  and  $D^+(\text{ads})$ . For adsorption involving adatoms and adions, the temperature must be high enough so that they can be formed. For simplicity, let



us imagine that each of the three kinds of ad-particles form a subsystem in the adsorbed phase. A subsystem indicates a particular variety of particles which are contained within the surface phase. At adsorption-desorption equilibrium, the number of ad-particles in each subsystem fluctuates about its own statistical mean value. We shall consider that the adsorbed surface phase is on the plane  $x = 0$ , as defined previously. Since adsorption and desorption of adions involves charge transfer, the number of electrons entering the solid at the plane  $x = 0$  resulting from the ionization of donors on the plane and the number of electrons leaving the solid at the plane  $x = 0$  for recombination with the adions must be equal. Otherwise there will be no adsorption-desorption equilibrium as represented by the symbolic Equation (5.9).

Now let us visualize the physical realities of the adsorption-desorption equilibrium process individually. For a concrete example, we shall consider the adsorption of hydrogen, which is a donor. Hydrogen may be adsorbed by the following process:



Let us imagine that the hydrogen molecules from the gas phase are striking the surface at a constant flux (molecules/cm<sup>2</sup> sec). Some of the hydrogen molecules are bounced back into the gas phase after collision with the surface, and others stay on the surface as H<sub>2</sub>(ads). Some of the adsorbed molecules may dissociate into two atoms, H(ads). One of the adatoms may migrate to another sub-area after dissociation. Among the adatoms some may become ionized as H<sup>+</sup>(ads) by donating electrons to the semiconductor. This process of adsorption is represented by the symbolic Equation (5.9a).

Continuing our visualization, the desorption process is the reverse of the adsorption process. During the visualization of the adsorption process, ad-particles are added to each subsystem in the

adsorbed phase every moment. To maintain dynamic equilibrium, the same number of ad-particles must be removed from each subsystem in the adsorbed phase in the same time interval.

Recalling Equation (5.9a), we visualize that some of the adions,  $H^+(\text{ads})$ , must be deionized by recombination with the electrons from underneath the plane  $x = 0$ , i. e., from the space charge layer of the semiconductor. Since the free electrons (or free holes), are not localized (see previous subsection), and every  $H^+(\text{ads})$  is an empty quantum state which has a finite probability to be occupied by an electron, the recombination process is as equally probable as the ionization process at a reversible equilibrium condition. If the probability of ionization and that of recombination are not equal, the adsorption-desorption process would not be in an equilibrium state, and kinetic processes must be considered instead of an adsorption isotherm.

Since the recombination process between  $H^+(\text{ads})$  and an electron can occur either when the adion is in motion or localized in a sub-area on the surface (a site), the reversible process of ionization and recombination does not require that the adions must be mobile. However the adatom, whether it is newly formed from the above described recombination process or not, must be able to migrate to another sub-area adjacent to another adatom in order to form  $H_2(\text{ads})$ . The distance of migration of an adatom,  $H(\text{ads})$ , before encountering another adatom is dependent on the surface concentration of adatoms. For very low concentrations, the average migration distance could be hundreds or thousands of lattice distances.

The newly formed  $H_2(\text{ads})$  is likely to desorb, because the association process is exothermic, and the newly formed  $H_2(\text{ads})$  has a higher energy level. At any rate  $H_2(\text{ads})$  will be desorbed statistically as fast as it is added to the subsystem in order to maintain the adsorption-desorption equilibrium.

Now let us ask: "What do we learn in the visualization of the adsorption-desorption process?"

We have learned that for the equilibrium process represented by the symbolic Equation (5.9), either the adion,  $D^+(\text{ads})$ , or the adatom  $D(\text{ads})$ , must be mobile to maintain the dynamic equilibrium between a three dimensional gas phase and the adions. Intuitively we may say that the adatom is mobile. Because adions are held by the coulombic force between the electrostatic charge and the space charge layer, therefore adions may be localized and immobile. A deeper consideration will show this may not be the case:

(1) Any one  $D^+(\text{ads})$  may fluctuate from  $D^+(\text{ads})$  to  $D(\text{ads})$  due to the random interaction with electrons in the space charge layer. If  $D(\text{ads})$  is mobile and becomes ionized, it may be slowed down by ejecting an electron to the solid, but the principle of momentum conservation should prevent it from going to a complete stop and becoming localized.

(2) Since we cannot differentiate one adion from another adion the random interaction with electrons may deionize one adion and at the same time another adion will be generated statistically. To an outside observer, the adions are mobile and arrange themselves in different patterns on the surface as time goes on.

(3) The coulombic force of the space charge layer will exert a restriction on the motion of the adions only when the adion moves away from the plane  $x = 0$ . Therefore on the plane  $x = 0$ , the adions are as free to move as the adatoms.

From these considerations we have no legitimate reason to assume that adions are localized. Since the above considerations (1) and (2) can equally apply to the adatoms, it is reasonable that both  $D(\text{ads})$  and  $D^+(\text{ads})$  are mobile. This, however, does not imply that their average mobilities are equal.

## Experimental Evidence

Direct observations on the migration of adatoms and adions are not lacking in the literature. A review on the direct investigations of the mobility of adatoms and adions has been given by Trapnell.<sup>(2c)</sup> One of the methods generally used in direct investigation of mobility of ad-particles is the field emission microscope. The principle of this method is that the emission current from a spot on the emitter is dependent on its local work function,  $\Phi_{th}$ , which is varied with the presence of adions or permanent dipoles as discussed in Chapter 4. Therefore, the field emission microscopic method directly investigates the migration of adions or permanent dipoles.

According to the data presented by Trapnell<sup>(2c)</sup> metal adions such as thorium, barium, and sodium begin to migrate on a tungsten surface at a temperature about 40 to 50% of its temperature of evaporation. On the basis of the two temperatures, Trapnell estimated that the activation energy of migration is about 40 to 50% of the energy of desorption. Naturally, if the adions are desorbed as ions, the activation energy of (adion) migration should be even less than the 40 to 50% of the energy of desorption, since the adions are held in the coulombic field and more energy is required for desorption. This has been shown by the data of cesium on tungsten.

Cesium on tungsten can be adsorbed as an ion and evaporated as an ion at low surface concentration,  $\theta$ . It can also be adsorbed as atoms and desorbed as atoms at higher surface concentrations, namely, when  $\theta > 1$ . Taylor and Langmuir<sup>(15, 16)</sup> reported that the energy of desorption of the cesium adion is a function of  $\theta$ , and the following values were given:

<u>Energy of desorption (ev)</u>	<u><math>\theta</math></u>
2.83 (65.2 Kcal)	0
1.93 (44.5)	0.67
1.77 (40.8)	1.0
0.79 (18.2)	2.0

where  $\theta = 1$  is defined as the concentration of  $3.563 \times 10^{14}$  particles/cm<sup>2</sup>.

The activation energy of surface migration is also a function of  $\theta$ . They reported that when  $0 \leq [Cs^+] \leq 2.73 \times 10^{13}/\text{cm}^2$ , the average activation energy of migration is 0.61 ev determined by measuring the surface migration constant (surface diffusion coefficient, as they called it) in a temperature interval from 654<sup>o</sup>K to 812<sup>o</sup>K. The migration coefficient is  $3.4 \times 10^{-5}$  cm<sup>2</sup>/sec. at 812<sup>o</sup>K.

For  $0 \leq [Cs^+] \leq 1.74 \times 10^{13}/\text{cm}^2$ , they determined only one value of migration coefficient; at 812<sup>o</sup>K it is  $1.4 \times 10^{-5}$  cm<sup>2</sup>/sec.

Assuming that the frequency factor of the migration coefficient is the same for the two surface ion concentrations, the average activation energy for migration at the lower surface ion concentration can be estimated by

$$\begin{aligned}
 E_m(\theta_2) &= E_m(\theta_1) + kT \ln \left\{ \frac{D_m(\theta_1)}{D_m(\theta_2)} \right\} \\
 &= 0.61 + 0.07 \times \ln \left( \frac{3.4}{1.4} \right) \\
 &= 0.67 \text{ ev}
 \end{aligned}$$

where  $E_m$  is the activation energy for migration, and  $D_m$  is the migration coefficient. From this estimation, the activation energy of migration of the adion,  $Cs^+$ , at low surface ion concentration, is only about one quarter of the activation energy of desorption as  $Cs^+$ . Therefore this confirms our previous prediction that when the adions are desorbed as

ions, the activation energy of adion migration should be less than 40 to 50% of the energy of desorption. It is interesting to note that, at  $\theta = 1$ , the activation energy of adion migration should be about  $1.77 \times \frac{0.67}{2.83} = 0.42$  ev; the average energy of desorption of a cesium atom on the second layer is 0.79 ev. Again if the activation energy of adion migration does not diminish in going from 1 monolayer to 2 monolayers, it is still only 50% of the energy of desorption of cesium as a monoatomic molecule.

The above-mentioned experimental observation shows that even if the desorbed particle (molecule) is different from the ad-particle in migration, the energy of desorption is still greater than the activation energy of migration. The aforementioned generalization by de Boer may still be valid.

The decrease of activation energy for migration of adions with increasing adion concentration is also evident from other data. Potassium adsorbed on tungsten has been studied in more detail. The activation energy of migration of the potassium ad-particle (probably ion), is 15.9 Kcal/gram-atom at a surface concentration of  $6 \times 10^{12}$  atoms/cm<sup>2</sup>; it decreases to 6.7 Kcal at  $4.8 \times 10^{14}$  atoms/cm<sup>2</sup>. (2c) Hydrogen on tungsten showed the same trend as cesium and potassium, as reported by Gomer, Wortman and Lundy. (17) This trend of experimental observations indicates that the static charge in the solid surface distributes itself in such a way that the restricting surface potential is tending to be equalized. This is nothing new, since it is a well known principle that the static charge tends to create an equipotential surface.

Two dimensional migration determined by local concentration variation has also been summarized by Trapnell. (2c) Sodium adsorbed on tungsten is reported to spread according to the relation

$$\frac{1}{C^2} = K(T) (t + t_0)$$

at  $0^{\circ}\text{C}$  where  $C$  is the surface concentration at a point of observation,  $K(T)$  is a function of temperature,  $t_0$  is a constant, and  $t$  is time. The activation energy of migration for low surface coverage conditions at about room temperature as determined by the above method is between 5.8 to 6.9 Kcal/gram-atom. The magnitude of the activation energy of migration and the above empirical equation which was shown to be a solution of the diffusion equation, suggests that the motion of the adsorbed sodium particle proceeds by an activation mechanism instead of by free translation on the tungsten surface.

Gomer, Wortman and Lundy<sup>(17)</sup> have used a field emission microscope to observe the surface migration of hydrogen at  $20^{\circ}\text{K}$  and  $180^{\circ}\text{K}$ . Their data showed that the activation energy of migration is about 10-20% of that of desorption. These agree well with the data presented by Trapnell for metals on tungsten. Furthermore, Trapnell<sup>(2d)</sup> has also reported that reversible chemisorption of hydrogen on tungsten occurs between  $-183^{\circ}\text{C}$  and  $0^{\circ}\text{C}$ . That is, at any temperature migration occurs easier than reversible adsorption, a fact which we wish to establish in conjunction with the formulation of the adsorption isotherms in this chapter.

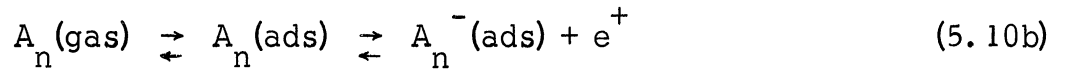
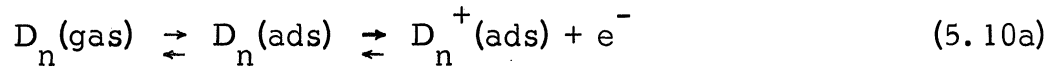
The data reported by Trapnell for the adsorbed sodium layer on tungsten<sup>(2c)</sup> can be used to check Hill's theory. If we take  $\phi^{\circ}$  to be 6.9 Kcal/gram-mole, then  $T = \phi^{\circ}/10k = 345^{\circ}\text{K}$ , which is greater than the observed temperature ( $273^{\circ}\text{K}$ ) at which the adsorbed sodium is mobile; therefore Hill's estimate is a little too conservative. However, if we take  $\phi^{\circ}$  as the minimum activation energy of migration, the data for sodium on tungsten gives  $\phi^{\circ} = 5.8$  Kcal/gram-atom, and the mobile temperature is about  $290^{\circ}\text{K}$  which is still higher than  $273^{\circ}\text{K}$ , but it is closer. Therefore, it is concluded that an ad-particle is certainly mobile at temperatures equal to or greater than  $\phi^{\circ}/10k$ , where  $\phi^{\circ}$  is the minimum activation energy of migration, but mobility may exist at even lower temperatures.

In view of the above theoretical as well as experimental aspects on the issue of localized or immobile adsorption vs. non-localized or mobile adsorption, it is more plausible that the ad-particles are mobile in the general adsorption-desorption equilibrium represented by Equation (5.9). At least the hypothesis of localized adsorption must be abandoned at temperatures equal or greater than  $\phi^0/10k$  as discussed above.

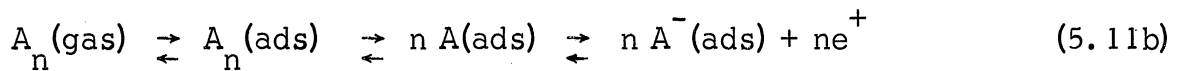
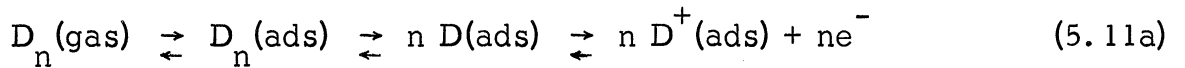
Presentation of A New Model  
for Adsorption Isotherms

It is postulated in this model that the gas phase is in equilibrium with several kinds of ad-particles on the surface of a semiconductor as defined above. The adsorption-desorption equilibria are represented by the following symbolic equations:

Adsorption-desorption equilibrium without dissociation:



Adsorption-desorption equilibrium with dissociation:



where  $e^-$  and  $e^+$  represent electrons and holes, respectively.

It is obvious that the case represented by Equation (5.10), can be regarded as a special case of Equation (5.11), namely,  $n \rightarrow 1$ . It goes without saying that Equations (5.10a), (5.11a) are for the adsorption-desorption equilibrium processes of a donor gas on a semiconductor surface, and Equations (5.10b), (5.11b) are that for an acceptor gas on a semiconductor surface.



To simplify our treatment, we shall consider in detail only the case of Equation (5.11a). As already mentioned each of the three kinds of ad-particles is regarded as a subsystem in the adsorbed surface phase. When temperatures and pressures of the system are such that the dynamic equilibrium represented by (5.11a) can be attained, the number of ad-particles in each subsystem will fluctuate about its statistical mean value. The instantaneous fluctuations of the number of particles in each of the subsystems of the adsorbed phase as well as the gas phase is due to exchange of particles between the subsystems in the dynamic equilibrium of the adsorption-desorption process.

In the light of the discussion in the previous sections we shall make the following basic assumptions:

(i) The semiconductor surface, approximated by the plane  $x = 0$  has a uniform Fermi level at the initial reference condition. The surface potential,  $Y_s$ , can be obtained by the solution of Poisson's equation in one dimension, namely the x-direction. From Chapter 2, in order for the non-degenerate semiconductor crystal surface to be approximated as a plane, its smallest dimension must be of the order of  $10^{-4}$  cm or more depending on the screening length,  $L_s$ , defined in Chapter 2.

(ii) The ad-particles are not localized. They have a greater or lesser degree of mobility. The translating motion of each kind of ad-particle may be hindered by a restricting potential energy function associated with the crystal surface. Such a restricting potential energy function, which has been originally proposed by Hill,<sup>(18)</sup> is of the following form for subsystem, j:

$$\phi_j(z, y) = (\phi_j^0/2) \left[ 2 - \cos \frac{2\pi y}{a} - \cos \frac{2\pi z}{a} \right] \quad (5.12)$$

where  $\phi_j^{\circ}$ , is the activation energy of migration for the ad-particle in subsystem "j". For simplicity we shall treat the square lattice only. It goes without saying several possible refinements are obvious. The path of migration is along the path of minimum energy barrier of the restricting potential energy function, Equation (5.12). The minimum point of the restricting potential energy function shall be decided from the following considerations.

Lennard-Jones<sup>(21)</sup> and co-workers have calculated the potential energy of an argon atom outside a (100) plane of a KCl crystal for the positions above a lattice point and above the mid-point of a square surface lattice. The results are presented in Figure 5.2 together with a similar calculation for a neon atom on a NaF crystal, also due to Lennard-Jones. The minimum points of potential energy in both cases are above the midpoint of the square lattice. This suggests that the minimum point of the restricting potential energy function is also located at the mid-point of a square lattice. Experimentally, Germer and Hartman<sup>(22)</sup> have reported that oxygen atoms on (100) planes of nickel arrange regularly on the centers of the square crystal surface lattice.

From the above experimental and numerical evidences, the minimum point of the restricting potential energy function of a square surface lattice, and the path of migration of an ad-particle are depicted in Figure 5.3 for the plane  $x = 0$ . The origin of the  $y-z$  coordinate system is chosen to be the mid-point of a square surface lattice. The path of minimum potential energy barrier can be shown to be along the lines  $y = na$ , or  $z = na$ , where "n" is zero or a positive integer. The energy barrier is  $\phi_j^{\circ}$  for the ad-particles in subsystem j. According to the evidence above the activation energy of migration,  $\phi_j^{\circ}$ , is dependent on the surface concentration (it has also been defined as surface coverage in Chapter 3).

This model is used in the remainder of this Chapter for the formulation of adsorption of neutral and charged particles on semiconductor surfaces.

FORMULATION OF EQUILIBRIUM ISOTHERMS  
FOR NEUTRAL PARTICLES

In this section, basic thermodynamic and statistical relationships are combined to derive quantitative mathematical expressions for the adsorption isotherms of neutral particles adsorbed on semiconductor surfaces. The following section will consider adsorption isotherms for ionized particles on semiconductor surfaces.

Basic Thermodynamic Relationships

In this section the basic thermodynamic concepts are reviewed for subsequent use in the quantitative formulation of the adsorption isotherms. Let

U	=	internal energy
T	=	absolute temperature, in K <sup>o</sup>
S	=	entropy
F = U - TS	=	the Helmholtz free energy
W	=	work
Q	=	heat
$\bar{\Psi}$	=	the generalized external field potential energy
V <sub>g</sub>	=	volume of the gas phase
$\mu_j = \left( \frac{\delta F}{\delta N_j} \right)_{S, V_g}$	=	the partial chemical potential of the jth subsystem, energy per particle
$\psi_j = \left( \frac{\delta \bar{\Psi}}{\delta N_j} \right)_{S, V_g}$	=	the partial generalized external potential of the jth subsystem in energy per particle
N <sub>j</sub>	=	number of particles in subsystem j
N	=	total number of particles.

When there is an external potential,  $\underline{\Psi}$ , the first law of thermodynamics takes the following form:

$$dU + d\underline{\Psi} = dQ - dW \quad (5.13)$$

From the second law of thermodynamics,

$$TdS \geq dQ \quad (5.14)$$

and combination with Equation (5.13) gives

$$TdS - (dU + d\underline{\Psi} + dW) \geq 0 \quad (5.15)$$

Under isothermal equilibrium conditions, and when there is no work performed either on or by the system, Equation (5.15) becomes,

$$d(TS - U - \underline{\Psi}) = 0 \quad (5.16)$$

or,

$$dF + d\underline{\Psi} = 0 \quad (5.17)$$

Let us consider that there are two subsystems, j and k, and a species, i, which exists in both subsystems j and k, and transfers from the j-subsystem into the k-subsystem, but the total number of particles of species i remains constant. The following relationships then exist

$$d(N_i)_j + d(N_i)_k = 0 \quad (5.18)$$

$$dF_i = (\mu_{ij} - \mu_{ik})dN_i \quad (5.19)$$

$$d\underline{\Psi}_i = (\psi_{ij} - \psi_{ik})dN_i \quad (5.20)$$

Combining Equations (5.17), (5.19) and (5.20), one obtains,

$$(\mu_{ij} + \psi_{ij}) = (\mu_{ik} + \psi_{ik}) \quad (5.21)$$

Having established Equation (5.21) the author will outline a procedure to evaluate the number of particles per unit volume or area in each phase and subsystem under equilibrium conditions.

### Basic Statistical Equilibrium Relationships

Since in this model the subsystems exchange particles among themselves, the Gibbs' distribution for a variable number of particles should be used. This distribution will lead to Fermi-Dirac as well as Bose-Einstein statistics as has been shown by Landau and Lifshitz. <sup>(19)</sup> Under the condition that

$$\exp (\mu_j - \epsilon_r) / kT \ll 1, \quad (5.22)$$

both Fermi-Dirac and Bose-Einstein distributions reduce to the Boltzmann distribution. Fowler and Guggenheim <sup>(20)</sup> have discussed this problem in detail and have shown that in applications to actual gases the Boltzmann distribution is applicable.

For a Boltzmann distribution the average number of particles,  $\bar{n}_{k,j}$ , in k-th quantum state in subsystem j has been shown <sup>(19a)</sup> to be

$$\bar{n}_{k,j} = \exp (\mu_j - \epsilon_k) / kT \quad (5.23)$$

where  $\mu_j$  is the chemical potential of the j-th subsystem and  $\epsilon_k$  is the energy associated with k-th quantum state.

From Equation (5.23) it follows that the total statistical average number of particles in subsystem j,  $N_j$ , can be written as

$$N_j = \exp (\mu_j / kT) \sum_k \exp (-\epsilon_k / kT) \quad (5.24)$$

If the motion of gas particles were governed by classical mechanics, the distribution function (5.23) over quantum states can be replaced by a distribution function of particles in phase space, i. e., over momenta and space coordinates. To do this, let  $dN_j$  be the average number of particles enclosed in the volume element of the phase space of j-th subsystem,  $d\mathcal{V}_j$ . But

$$d\mathcal{V}_j = dx_1 \dots dx_s d(m_j v)_1 \dots d(m_j v)_s = m_j^s dx_1 \dots dx_s dv_1 \dots dv_s$$

where

- $s$  = number of degrees of freedom
- $x_1$  = space coordinates, as  $x, y, z$
- $(m_j v)_1$  = momentum coordinates in the direction,  $x_1$
- $m_j$  = mass of particle in subsystem  $j$ .

In terms of a distribution in classical phase space,  $dN_j$  is written<sup>(19a)</sup> as

$$dN_j = \exp(\mu_j/kT) \exp[-\epsilon(x_1, m_j v_1)/kT] h^{-s} d\tau_j \quad (5.23a)$$

where  $\epsilon(x_1, m_j v_1)$  is the energy of a particle as a function of the space coordinates and momenta in subsystem  $j$ ;  $h$  is the Plank's constant. The total average number of particles in subsystem  $j$  is obtained by integrating Equation (5.23a).

$$N_j = \exp(\mu_j/kT) h^{-s} \int \dots \int_{(2s\text{-fold})} \exp(-\epsilon/kT) d\tau_j = \lambda_j f_j \quad (5.24a)$$

where

$$\lambda_j = \exp(\mu_j/kT) \quad (5.24b)$$

$$f_j = h^{-s} \int \dots \int_{(2s\text{-fold})} \exp(-\epsilon/kT) d\tau_j \quad (5.24c)$$

which is the partition function of a particle in subsystem  $j$ .

It is appropriate to point out that Equation (5.23) and (5.23a) are equivalent, and so are Equations (5.24) and (5.24a). Equation (5.24c) gives the classical definition of the partition function of a particle in subsystem  $j$ , the equivalent definition for quantum statics is usually written as the following

$$f_j = \sum_k \exp(-\epsilon_k/kT) \quad (5.24d)$$

With these relationships the equilibrium isotherms between the various subsystems can now be obtained.

### Derivation of Adsorption Isotherms for Neutral Particles

For convenience, the various types of particles, or subsystems, defined in Equations (5.11) are labelled as follows:

$j = 1$ , = gas phase, which is also regarded as a subsystem, since it is in equilibrium with subsystem 2.

$j = 2$ , =  $D_n$  (ads), or  $A_n$  (ads), adsorbed molecular subsystem.

$j = 3$ , =  $nD$  (ads) or  $nA$  (ads), adsorbed atomic subsystem.

$j = 4$ , =  $nD^+$  (ads) or  $nA^-$  (ads), adsorbed ionic subsystem.

### Equilibrium Relationship Between Gas Phase and Subsystem 2.

From Equation (5.21), for species in subsystems 1 and 2, one obtains

$$\mu_1 + \psi_1 = \mu_2 + \psi_2 \quad (5.21a)$$

That is

$$\exp \frac{\mu_1 + \psi_1}{kT} = \exp \frac{\mu_2 + \psi_2}{kT}$$

From Equation (5.24b) it follows that

$$\lambda_2 = \lambda_1 \exp \left[ (\psi_1 - \psi_2)/kT \right]$$

Let

$w_2 = \psi_1 - \psi_2$  = the energy of adsorption accompanying the formation of a Van der Waal's bond, as a molecule goes from the lowest free state in the gas and the lowest adsorbed state on the surface, without dissociation or ionization. [See Figure 5.3.] (It is noted that if, in the range considered, the Van der Waal's force is an attractive force,  $w_2$  will be positive and heat will be evolved upon adsorption.) Therefore

$$\lambda_2 = \lambda_1 \exp \left[ w_2/kT \right] \quad (5.25)$$

From Equation (5.24a) by definition

$$\lambda_j = \frac{N_j}{f_j}$$

Therefore the relationship between the average number of particles in subsystems 1 and 2 is given by

$$N_2 = N_1 (f_2/f_1) \exp [w_2/kT] \quad (5.26)$$

In order to express this relationship in more useful form, it is now necessary to express  $f_1$  and  $f_2$  in terms of other definable quantities. The partition function of a three dimensional gas is given in any standard textbook of statistical physics. For the partition function of free particles in a volume

$$f_1 = \left[ \frac{2\pi m_1 kT}{h^2} \right]^{3/2} I_1 V_g \quad (5.27)$$

where

$I_1$  = internal partition function of gas molecule.

The partition function for an ad-particle in subsystem 2,  $f_2$ , with two degrees of freedom of migration in a restricting potential energy function can be formulated by following a procedure due to Hill.<sup>(18)</sup> The restricting potential energy function is represented by Equation (5.12).

The classical partition function of an ad-particle in subsystem,  $j$ , in a two dimensional space, i. e., the plane  $x = 0$  can be written from Equation (5.24c) for  $s = 2$ .

$$f_{j \text{ class}} = \frac{m_j^2}{h^2} \iint_{-\infty}^{\infty} \iint_0^L \exp (-\epsilon/kT) dy dz dv_y dv_z \quad (5.28)$$

where

$$\epsilon = (1/2) m_j (v_y^2 + v_z^2) + (1/2) \phi_j^0 \left( 2 - \cos \frac{2\pi y}{a} - \cos \frac{2\pi z}{a} \right) \quad (5.29)$$



The integration over the momenta extends from  $-\infty$  to  $\infty$ . It can easily be performed by changing into polar coordinates.

$$f_{j \text{ class}} = \frac{2\pi m_j kT}{h^2} \exp(-\Phi_j^0/kT) \left[ \int_0^L \exp\left(\frac{\Phi_j^0}{2kT} \cos \frac{2\pi y'}{a}\right) dy' \right]^2 \quad (5.30)$$

For the integration of,

$$\int_0^L \exp\left[\frac{\Phi_j^0}{2kT} \cos\left(\frac{2\pi y'}{a}\right)\right] dy'$$

let

$$\Theta = \frac{2\pi y'}{a}$$

Since  $a$ , the lattice constant, is small,  $L$  is a macroscopic linear distance, we let  $L = na$  where  $n$  is an integer,

$$\begin{aligned} \text{when } y' = 0 & \quad \Theta = 0 \\ y' = na = L & \quad \Theta = 2n\pi \end{aligned}$$

$$dy' = \frac{a}{2\pi} d\Theta$$

Therefore the above integral becomes

$$\begin{aligned} & \frac{a}{2\pi} \int_0^{2n\pi} \exp\left(\frac{\Phi_j^0}{2kT} \cos \Theta\right) d\Theta \\ &= \frac{na}{2\pi} \int_0^{2\pi} \exp\left(\frac{\Phi_j^0}{2kT} \cos \Theta\right) d\Theta \\ &= \frac{L}{2\pi} \int_0^{2\pi} \exp\left(\frac{\Phi_j^0}{2kT} \cos \Theta\right) d\Theta \\ &= \frac{L}{2\pi} \int_0^{2\pi} \exp\left(-\frac{\Phi_j^0}{2kT} \cos \Theta\right) d\Theta = L I_0(\Phi_j^0/2kT) \end{aligned}$$

It can be recognized that the last integral is the integral representation of a modified Bessel function of the first kind,  $2\pi I_0\left(\frac{\Phi_j^0}{2kT}\right)$ . Therefore Equation (5.30) can be written,

$$f_{j \text{ class}} = \left(\frac{2\pi m_j kT}{h^2}\right) L^2 I_0^2\left(\frac{\Phi_j^0}{2kT}\right) \exp(-\Phi_j^0/kT) \quad (5.31)$$

We shall combine the vibrational and rotational partition functions with the classical partition function represented by Equation (5.31).

Let  $I_j$  = product of all internal partition functions of ad-particles in subsystem  $j$ . Then the partition function of an ad-particle, in subsystem,  $j$ , migrating in a two dimensional space, i. e., on the plane  $x = 0$  is

$$f_j = I_j f_{j \text{ class}} = I_j \left(2\pi m_j kT/h^2\right) L^2 I_0^2\left(\frac{\Phi_j^0}{2kT}\right) \exp(-\Phi_j^0/kT) \quad (5.32)$$

It should be pointed out that the assumed potential energy function of a simple cubic surface lattice is a simplest case, and several possible generalizations will be obvious. Since we are mainly pursuing the general trend of mobile adsorption, side issues will be omitted.

It should be pointed out further that  $\Phi_j^0$  is a function of surface coverage (or surface concentration). It can be shown that when  $\Phi_j^0 \rightarrow 0$ , the partition function (5.32) reduces to free translation,

$$\left(\frac{2\pi m_j kT}{h^2}\right) L^2 I_j.$$

For convenience of representation we shall define a restricting coefficient,  $r_j$ , by the following relation:

$$r_j = I_0^2\left(\frac{\Phi_j^0}{2kT}\right) \exp(-\Phi_j^0/kT) \quad (5.33)$$

Then Equation (5.31) can be simplified to

$$f_j = \left(\frac{2\pi m_j kT}{h^2}\right) L^2 I_j r_j \quad (5.34)$$

For further simplification, we shall let

$$\begin{aligned}
 m &= \text{atomic weight of } [D], \text{ or } [A] \\
 n &= \text{number of atoms per molecule} \\
 V_g &= \text{total gas volume in the system, cm}^3 \\
 \beta &= \left( \frac{2\pi mkT}{h^2} \right) \text{ (in cm}^{-2}\text{)} \quad (5.35)
 \end{aligned}$$

$$S_A = L^2 = \text{total adsorbing semiconductor area in the system, cm}^2.$$

Then the partition function in the gas phase given by Equation (5.27) can also be written as

$$f_1 = (n\beta)^{3/2} I_1 V_g \quad (5.27a)$$

and the partition function for an ad-particle of species  $i$  in subsystem 2 of the surface phase is

$$f_2 = (n\beta) I_2 r_2 S_A \quad (5.34a)$$

Combining Equations (5.26), (5.27a), and (5.34a) one obtains

$$\frac{N_2}{S_A} = \frac{N_1}{V_g} \left( \frac{I_2 r_2}{I_1} \right) \left( \frac{1}{n\beta} \right)^{1/2} \exp w_2/kT \quad (5.36)$$

For the ideal gas approximation

$$PV_g = N_1 kT$$

or the particle concentration in the gas phase is

$$\left( \frac{N_1}{V_g} \right) = \left( \frac{P}{kT} \right) \quad (5.37)$$

For the sake of avoiding confusion in units it is defined that  $P$  is in dynes/cm<sup>2</sup>,  $kT$  in ergs, and volume in cm<sup>3</sup>. Then  $(P/kT)$  is in cm<sup>-3</sup>. Combining Equations (5.36) and (5.37), and writing  $[D_n]$ , or  $[A_n]$  for  $N_2/S_A$ , number of particles per cm<sup>2</sup>:

$$[D_n] = \left(\frac{P}{kT}\right) \left(\frac{I_2 r_2}{I_1}\right) \left(\frac{1}{n\beta}\right)^{1/2} \exp(w_2/kT) \quad (5.38a)$$

or

$$[A_n] = \left(\frac{P}{kT}\right) \left(\frac{I_2 r_2}{I_1}\right) \left(\frac{1}{n\beta}\right)^{1/2} \exp(w_2/kT) \quad (5.38b)$$

These are adsorption isotherms, relating the concentration of molecular species on the surface to the partial pressure of the species in the gas phase.

It is appropriate to point out here that the use of the perfect gas law, Equation (5.37), restricts the validity of the derived isotherms to the temperatures and pressures, in which the perfect gas law is valid. Several obvious refinements are possible, such as the introduction of a compressibility factor to accommodate deviations from perfect gas behavior. Since these represent deviations from the intent of this work they will not be pursued further at this time.

#### Equilibrium Relationships Between Subsystems 2 and 3, and 1 and 3

In entering subsystem 3, the molecule  $D_n$  or  $A_n$  dissociates into  $n$  atoms, and the total energy of the particles in subsystem 1, and 2 now is comprised of a chemical energy associated with each particle,  $\mu_3$ , a generalized external field energy per atom,  $\psi_3$ , and an energy of dissociation per atom,  $\Delta$ . This can be expressed as

$$\mu_1 + \psi_1 = \mu_2 + \psi_2 = n\mu_3 + n\psi_3 + n\Delta \quad (5.39)$$

where

$\Delta$  = dissociation energy per atom which is also a form of potential energy.

Following the procedure as outlined above, define

$$nw_3 \equiv \psi_1 - n\psi_3 \quad (5.40)$$

Now substitution of Equation (5.40) into Equations (5.24a) and (5.39) gives the relationship

$$\lambda_3 = \lambda_1 \frac{1}{n} \exp \left[ \frac{w_3 - \Delta}{kT} \right] \quad (5.41)$$

Substitution for the  $\lambda$ 's gives

$$\frac{N_3}{f_3} = \left( \frac{N_1}{f_1} \right) \frac{1}{n} \exp \left[ \frac{w_3 - \Delta}{kT} \right] \quad (5.42)$$

Now, define the partition functions for the atoms on the surface in subsystem 3

$$f_3 = \left( \frac{2\pi mkT}{h^2} \right) I_3 r_3 S_A = \beta I_3 r_3 S_A \quad (5.43)$$

Substitution of Equations (5.43), (5.37) and (5.27a) into Equation (5.42) gives an expression for  $N_3/S_A$ . But since  $N_3/S_A$  is the surface concentration of atoms in subsystem 3, then for donor atoms, the result can be written as

$$N_3/S_A = [D] = \frac{\beta I_3 r_3}{n \sqrt{(n\beta)^{3/2} I_1}} \exp \left[ \frac{w_3 - \Delta}{kT} \right] \left[ \frac{P_D}{kT} \right]^{1/n} \quad (5.44a)$$

For acceptor atoms on the surface in subsystem 3, the result is

$$[A] = \frac{\beta I_3 r_3}{n \sqrt{(n\beta)^{3/2} I_1}} \exp \left[ \frac{w_3 - \Delta}{kT} \right] \left[ \frac{P_A}{kT} \right]^{1/n} \quad (5.44b)$$

Equations (5.44a) and (5.44b) relate the concentration of dissociated atoms on the surface coming from an n-atom molecule, to the dissociation energy, the partial pressure of the molecular gas, and other factors as indicated.

FORMULATION OF ADSORPTION ISOTHERMS  
FOR CHARGED PARTICLES

In the previous section, the adsorption isotherms for neutral particles have been formulated. The adsorption isotherms for charged ad-particles, i. e., adions, will be formulated in this section. We shall approach the problem first by considering the equilibrium relationships between the subsystems 3 and 4 defined previously. Then, the adsorption isotherms for charged particles will be derived by using the adsorption isotherms for adatoms in subsystem 3, defined in Equations (5.44a) and (5.44b) above.

Equilibrium Relationships Between  
Subsystem 3 and Subsystem 4

The adsorbed atoms in subsystem 3 acting as donors or acceptors on a semiconductor surface are assumed to be in equilibrium with their ions, in the same manner as if they were impurity centers in the bulk of a semiconductor. The equilibrium concentrations of neutral and charged particles are determined by the Fermi level at the surface. This has been assumed by Krusemeyer and Thomas,<sup>(9)</sup> and others<sup>(3, 4, 11)</sup> mentioned previously.

For a donor gas, it is assumed that the neutral adsorbed donor atom such as a hydrogen atom has an uncompensated electron spin. Therefore in going from subsystem 3 to subsystem 4 the following reactions can occur:



Since the electrons initially are in a surface donor state with energy level  $E_d$ , then the distribution function is given by<sup>(12b)</sup>

$$\frac{[D]}{[D] + [D^+]} = \frac{1}{1 + \frac{1}{2} \exp [(E_d - E_F - Y_{s, eq})/kT]} \quad (5.46)$$

where  $Y_{s, eq}$  is the surface potential energy under equilibrium conditions.

From Equation (5.46) the following equation is obtained.

$$[D] = 2 [D^+] \exp [(E_F + Y_{s, eq} - E_d)/kT] \quad (5.47)$$

Since  $E_F$  and  $E_d$  refer to the initial conditions, they are constant in the Equations (5.46) and (5.47). Further it is customarily assumed that  $E_d$  relative to  $E_c$  remains constant, namely

$$E_c = E_d + \epsilon_d \quad (5.48)$$

Therefore

$$\begin{aligned} E_F - E_d &= (E_F - E_{c, B}) + (E_{c, B} - E_d) \\ &= -\phi_{n, B} + \epsilon_d \\ &= -(\phi_{n, B} - \epsilon_d) \end{aligned} \quad (5.49)$$

By substitution of Equation (5.49) into Equation (5.47) the following equation is obtained,

$$[D] = 2 [D^+] \exp [Y_{s, eq}/kT] \exp [(\epsilon_d - \phi_{n, B})/kT] \quad (5.47a)$$

The Equations (5.48) and (5.49) are illustrated in Figure 5.4b for both the customary point of view and in Figure 5.4c for the equivalent point of view suggested in Chapter 4.

For the acceptor gas, it is assumed that the A atom has all electron spins compensated. When these atoms ionize into  $[A^-]$ , an electron of either spin can be accepted. That is



where  $e_v^+$  is a hole in the valence band at the semiconductor surface. Therefore, the distribution function is given by, (12b)

$$\frac{[A^-]}{[A] + [A^-]} = \frac{1}{1 + \frac{1}{2} \exp \left[ \frac{E_A - (E_F + Y_{s,eq})}{kT} \right]} \quad (5.51)$$

It follows that

$$[A] = \frac{1}{2} [A^-] \exp \left[ \frac{(E_A - E_F - Y_{s,eq})}{kT} \right] \quad (5.52)$$

where  $[A^-]$  is the total singly charged acceptor ion concentration;  $E_A$  the acceptor level associated with the adatom  $[A]$ , on the surface, which is constant relative to  $E_v(0)$ ; and  $E_F$  is the Fermi level at the initial condition. The situation is similar to the previous case with donors on the surface except that  $Y_{s,eq}$  now is negative by the convention of Chapter 2. At the initial condition,

$$\begin{aligned} E_A - E_F &= (E_A - E_{v,B}) + (E_{v,B} - E_F) \\ &= \epsilon_A - \phi_{p,B} \\ &= -(\phi_{p,B} - \epsilon_A) \end{aligned} \quad (5.53)$$

and

$$Y_{s,eq} = -Y'_{s,eq} \quad (5.54)$$

Therefore it follows that,

$$[A] = \frac{1}{2} [A^-] \exp \left[ \frac{Y'_{s,eq}}{kT} \right] \exp \left[ \frac{(\epsilon_A - \phi_{p,B})}{kT} \right] \quad (5.52a)$$

Equations (5.47a) and (5.52a) are our desired relationships between the particles in subsystem 3 and subsystem 4, for donors and acceptors, respectively. Now, we consider the variation of the ratio,  $[D] / [D^+]$  as temperature or  $Y_s$  varies for various cases.

From Equation (5.47a), the ratio,  $[D] / [D^+]$  can be written



$$[D] / [D^+] = 2 \exp(Y_s/kT) \exp[(\epsilon_d - \phi_{n,B})/kT] \quad (5.47b)$$

When  $Y_s$  increases,  $[D] / [D^+]$  increases for a given semiconductor and temperature; i. e., fewer atoms become ionized at higher temperature.

For the ratio,  $[A] / [A^-]$ , the trend of variations is similar to the above case for donors.

The exact relationship between  $[D]$  and  $[D^+]$ , and that of  $[A]$  and  $[A^-]$  can be obtained by eliminating  $Y_{s,eq}$  and  $Y'_{s,eq}$  from Equations (5.47a) and (5.52a) respectively. This can be carried out by using the relationships between  $Y_{s,eq}$  or  $Y'_{s,eq}$  and  $\Sigma_{\square}^{\pm}$ , which were derived in Chapter 2. The factors  $\Sigma_{\square}^{\pm}$  are the total surface charges which are related to  $[D^+]$  and  $[A^-]$  by the following relations:

$$\Sigma_{\square}^+ = [D^+] \pm [F^{\pm}] \quad (4.34)$$

and

$$\Sigma_{\square}^- = [A^-] \pm [F^{\mp}] \quad (4.35)$$

For the convenience of presentation, we shall divide it into two classes according to the nature of the space charge region generated upon adsorption with charge transfer. The first class of cases (Class I) is associated with accumulation layers on intrinsic or extrinsic semiconductors, and with highly inverted surface layers on nearly intrinsic semiconductors. The second class of cases (Class II) is associated with a depletion region or slightly inverted space charge region.

The Class I cases are discussed first and the adsorption isotherms are derived completely before the Class II cases are considered.

### Class I Cases: Adsorption Associated with Accumulation Space

#### Charge Regions.

In the following development of equilibrium relationships, we shall represent the case of  $[D^+]$  and  $[D]$  in detail. For the case of

$[A^-]$  and  $[A]$  only the final result is given because of the similarity of the two groups of cases. The equations from the previous chapters which are to be used in further development are summarized.

$$Y_s \equiv -Y'_s = u_s kT$$

for an intrinsic semiconductor

$$\sinh(u_s/2) = (L_m/n_i)^{1/2} \Sigma_D^+/2 \quad (2.19)$$

for an n-type semiconductor

$$\sinh(u_s/2) \approx (L_m/n_B)^{1/2} \Sigma_D^+/2 \quad (2.35)$$

and

$$[D] = 2[D^+] \exp(u_s) \exp[(\epsilon_d - \phi_{n,B})/kT] \quad (5.47c)$$

From Equations (2.19), (2.35), (4.34) and (5.47c), it is clear that the relationships between  $[D]$  and  $[D^+]$  can be expressed explicitly only when  $u_s < 1$ , and when  $u_s > 2$ . For the intermediate case, a numerical solution is required. We shall treat the case  $u_s < 1$ , and  $u_s > 2$  in the following analytical formulations.

Case (I.1), for  $0 \leq u_s < 1$ .

Under this condition, Equations (2.19), (2.35), and (5.47c) can be approximated by the following relations,

$$\sinh(u_s/2) \approx u_s/2 \approx (L_m/n_i)^{1/2} \Sigma_D^+/2 \quad (5.55)$$

and

$$u_s/2 \approx (L_m/n_B)^{1/2} \Sigma_D^+/2 \quad (5.56)$$

Furthermore, for  $u_s < 1$ , then

$$\exp(u_s) = 1 + u_s \quad (5.57)$$

By combining Equations (5.47c), (5.56), (5.57) and (4.34) the following equation is obtained

$$\begin{aligned}
[D] &= 2 \exp [-(\Phi_{n, B} - \epsilon_d)/kT] (1 + u_s) [D^+] \\
&= 2 \exp [-(\Phi_{n, B} - \epsilon_d)/kT] \\
&\quad \left\{ 1 + (L_m/n_B)^{1/2} ([D^+] \pm [F^\pm]) \right\} [D^+] \quad (5.58a)
\end{aligned}$$

For donors on an intrinsic semiconductor, the term  $n_B$  must be replaced by  $n_i$ , and  $\Phi_{n, B}$  becomes equal to  $E_g/2$ . Such an equation is omitted. Equation (5.58a) shows that when  $u_s$  is very small, then  $[D]$  and  $[D^+]$  are proportional to each other. The corresponding equilibrium relationship for  $[A]$  and  $[A^-]$  on an intrinsic or p-type semiconductor is given as

$$\begin{aligned}
[A] &= \frac{1}{2} \exp [-(\Phi_{p, B} - \epsilon_A)/kT] \\
&\quad \left\{ 1 + (L_m/p_B)^{1/2} ([A^-] \pm [F^\mp]) \right\} [A^-] \quad (5.58b)
\end{aligned}$$

Case (I. 2), for High Surface Coverage,  $u_s > 2$ .

For a high surface coverage of adsorbed ions, the normalized surface potential is greater than 2, and Equations (2.19) and (2.35) can be approximated by,

$$u_s \approx \ln \left[ \frac{L_m}{n_i} (\Sigma_D^+)^2 \right] \quad (5.59)$$

and for an n-type semiconductor

$$u_s \approx \ln \left[ \frac{L_m}{n_B} (\Sigma_D^+)^2 \right] \quad (5.60)$$

Under the condition that  $u_s > 2$ , the surface potential is determined by  $[D^+]$ , and the concentration of fast states  $[F^\pm]$  appears to be small, as discussed and established in Chapter 4. Consequently Equation (4.34) can be approximated by

$$\Sigma_D^+ \approx [D^+] \quad (5.62)$$

For convenience of representation we shall further divide this case into several sub-cases.

Subcase (I. 2a). High Coverage on an Intrinsic Semiconductor.

Here again, we shall give the detailed analysis only for donors on an intrinsic semiconductor. The results of acceptors on an intrinsic semiconductor are given by analogy.

Since for an intrinsic semiconductor  $\phi_{n, B} = \phi_{i, B}$ , combinations of Equations (5.47c), (5.59) and (5.62) give the following equation.

$$[D] \approx 2 (L_m/n_i) [D^+]^3 \exp [(\epsilon_d - \phi_{i, B})/kT] \quad (5.63)$$

Furthermore, since

$$\begin{aligned} n_i = p_i &= 2 (2\pi kT/h^2)^{3/2} (m_n m_p)^{3/4} \exp (-\phi_{i, B}/kT) \\ &= (N_c N_v)^{1/2} \exp (-\phi_{i, B}/kT) \end{aligned}$$

therefore, Equation (5.63) can be written

$$[D] \approx 2 (L_m^2/N_v N_c)^{1/2} [D^+]^3 \exp (\epsilon_d/kT) \quad (5.63a)$$

Similarly for acceptors on an intrinsic semiconductor

$$[A] \approx \frac{1}{2} (L_m^2/N_v N_c)^{1/2} [A^-]^3 \exp (\epsilon_A/kT) \quad (5.63b)$$

For simplification, we shall let

$$C_{i, D} = 2 (L_m^2/N_v N_c)^{1/2} \exp (\epsilon_d/kT) \quad (5.64a)$$

and

$$C_{i, A} = \frac{1}{2} (L_m^2/N_v N_c)^{1/2} \exp (\epsilon_A/kT) \quad (5.64b)$$

Then Equations (5.63a) and (5.63b) can be simplified to

$$[D] \approx C_{i, D} [D^+]^3 \quad (5.65a)$$

and

$$[A] \approx C_{i, A} [A^-]^3 \quad (5.65b)$$

Subcase (I. 2b), High Coverage of Donors on an n-Type Semiconductor or  
Acceptors on a p-Type Semiconductor.

From Equation (5.63) by replacing subscript  $i$  with subscript  $n$ , it follows that

$$[D] \cong 2(L_m/n_B) [D^+]^3 \exp (\epsilon_d - \Phi_{n,B})/kT \quad (5.66)$$

Furthermore, since

$$n_B = N_C \exp [-\Phi_{n,B}/kT]$$

then

$$[D] \cong (2L_m/N_C) [D^+]^3 \exp (\epsilon_d/kT) \quad (5.66a)$$

Similarly for acceptors on a p-type semiconductor the result is

$$[A] \cong (L_m/2N_V) [A^-]^3 \exp (\epsilon_A/kT) \quad (5.66b)$$

For simplification, we shall define

$$K_n = (2L_m/N_C) \exp (\epsilon_d/kT) \quad (5.67)$$

$$K_p = (L_m/2N_V) \exp (\epsilon_A/kT) \quad (5.68)$$

and Equations (5.66a) and (5.66b) can be written as

$$[D] \cong K_n [D^+]^3 \quad (5.69a)$$

$$[A] \cong K_p [A^-]^3 \quad (5.69b)$$

These equations were used in Chapter 4 as Equation (4.51a).

Class II Cases: Adsorption Associated with Depletion-Inversion Space  
Charge Regions.

Under this heading, the cases of surface donors on a p-type semiconductor and surface acceptors on an n-type semiconductor are included. We shall formulate, as the previous subsection, the equilibrium relationships between  $[D]$  and  $[D^+]$ . The relationships between  $[A]$  and  $[A^-]$  are given by analogy.

The cases to be treated in this subsection are those in which  $u_s$  can be approximately represented by an explicit function of  $\Sigma_D^+$  obtained in Chapter 2. That is, for low coverage (slight depletion layer),  $u_s \leq 0.9$

$$u_s \approx \left[ \frac{2L_m}{n_B + p_B} \right]^{1/2} \Sigma_D^+ \quad (2.46)$$

for moderate coverage (depletion-inversion layer),  $2 < u_s < (2 u_B' - 1)$

$$u_s = 1 + \left[ \frac{L_m}{p_B} (\Sigma_D^+)^2 \right] \quad (2.50)$$

or alternatively, over the interval  $u_B' - 1 < u_s < 2 u_B' + 1$

$$u_s = (\text{slope}) (L_m/p_B)^{1/2} \Sigma_D^+ - (\text{intercept}) \quad (2.71)$$

and for very high coverage (strong inversion layer),  $u_s > u_c$

$$u_s = 2 u_B' + \ln \left[ \frac{L_m}{p_B} (\Sigma_D^+)^2 \right] \quad (2.67)$$

These different space charge regions represent different degrees of relative surface ion coverage.

Case (II. 1), Low Surface Ion Coverage,  $u_s < 1$ .

This case is analogous to Case (I. 1). We shall use the approximations from Equations (4.34) and (5.56). By combining Equations (2.46), (5.57), and (4.34) the following equation is obtained.

$$[D] = 2 \exp \left\{ -(\Phi_{n,B} - \epsilon_d)/kT \right. \\ \left. \left\{ [D^+] + \left[ \frac{2L_m}{n_B + p_B} \right]^{1/2} ([D^+] \pm [F^\pm]) [D^+] \right\} \right\} \quad (5.70a)$$

The corresponding equilibrium relationships between  $[A]$  and  $[A^-]$  on an n-type semiconductor is given,

$$[A] = \frac{1}{2} \exp \left( -(\Phi_{p, B} - \epsilon_A)/kT \right)$$

$$\left\{ [A^-] + \left[ \frac{2L_m}{n_B + p_B} \right]^{1/2} ([A^-] \pm [F^+]) [A^-] \right\} \quad (5.70b)$$

Case (II.2), Intermediate Surface Ion Coverage Associated with a Depletion-Inversion Space Charge Region.

In Chapter 2, equivalent approximations for  $u_s$  vs. function of  $\Sigma_D^\pm$  are obtained for this case. The linear approximation, represented by Equation (2.71) is more tractable, and it has been checked by experimental observations presented in Chapter 4. Consequently, we shall use Equation (2.71) for further development. For convenience we shall rewrite Equation (2.71) in the following form

$$u_s = m' \left[ \left( \frac{L_m}{p_B} \right)^{1/2} (\Sigma_D^+) \right] - b \quad (5.71)$$

where  $m'$  is the slope to be computed from Equation (2.74), namely

$$m' = \frac{\left[ \left( \frac{L_m}{p_B} \right)^{1/2} (\Sigma_D^+) \right]^* \exp u_B'}{\sinh u_B' + \sinh (u_s^* - u_B')} \quad (5.72)$$

and  $b$  is the intercept given in the following,

$$b = u_s^* - m' \left[ \left( \frac{L_m}{p_B} \right)^{1/2} (\Sigma_D^+) \right]^* \quad (5.72a)$$

where  $u_s^*$  and  $\left[ \left( \frac{L_m}{p_B} \right)^{1/2} (\Sigma_D^+) \right]^*$  have been defined in Chapter 2.

To obtain the equilibrium relationship between  $[D]$  and  $[D^+]$  we shall proceed as follows. From Equation (5.47e) and the relations,

$$\Phi_{n, B} = E_g - \Phi_{p, B}$$

$$N_V/p_B = \exp (\Phi_{p, B}/kT),$$

it follows that

$$[D] = 2 [D^+] \exp(u_s) \left(\frac{N_v}{p_B}\right) \exp\left[\frac{\epsilon_d - E_g}{kT}\right] \quad (5.73)$$

Combining Equations (5.73), (5.72), (5.71), and (5.62), the following relation is obtained

$$[D] \cong 2 (N_v/p_B) \exp[-b + (\epsilon_d - E_g)/kT] [D^+] \exp\left[m' (L_m/p_B)^{1/2} [D^+]\right] \quad (5.73a)$$

The corresponding relations for acceptors on n-type are given:

$$[A] \cong \frac{1}{2} (N_c/n_B) \exp[-b + (\epsilon_A - E_g)/kT] [A^-] \exp\left[m' (L_m/n_B)^{1/2} [A^-]\right] \quad (5.73b)$$

Equation (5.73a) can be written in dimensionless form by multiplying both sides by  $m' (L_m/p_B)^{1/2}$

$$[D] m' (L_m/p_B)^{1/2} = 2 (N_v/p_B) \exp[-b + (\epsilon_d - E_g)/kT] m' (L_m/p_B)^{1/2} [D^+] \exp\left[m' (L_m/p_B)^{1/2} [D^+]\right]$$

For simplification, let

$$H_{p,d} = 2 (N_v/p_B) \exp[-b + (\epsilon_d - E_g)/kT] \quad (5.74)$$

and

$$B_p = m' (L_m/p_B)^{1/2} \quad (5.75)$$

Then

$$B_p [D] \cong H_{p,d} B_p [D^+] \exp\left\{B_p [D^+]\right\} \cong H_{p,d} \exp\left\{B_p [D^+] + \ln(B_p [D^+])\right\} \quad (5.75a)$$

Therefore Equation (5.73a) can be written

$$B_p [D^+] + \ln B_p [D^+] \cong \ln\left\{B_p [D]/H_{p,d}\right\} \quad (5.76a)$$



Now for acceptors on an n-type semiconductor let

$$B_n = m' (L_m/n_B)^{1/2} \quad (5.77)$$

$$H_{n,A} = \frac{1}{2} (N_c/n_B) \exp [-b + (\epsilon_A - E_g)/kT] \quad (5.78)$$

Equation (5.73b) can be written

$$B_n [A^-] + \ln B_n [A^-] \approx \ln \left\{ B_n [A] / H_{n,A} \right\} \quad (5.76b)$$

### Case (II. 3), Surface Ion Coverage Associated with a Strong Inversion

#### Space Region.

In this case

$$u_s \approx 2 u_B' + \ln \left[ (L_m/p_B) (\Sigma_D^+)^2 \right] \approx u_c \quad (2.67a)$$

For donors on p-type semiconductor, which is only slightly p-type the space charge region is strongly inverted. If we write Equation (2.67a) in terms of minority carrier,  $n_B$ , the following equation is obtained

$$u_s \approx \ln \left[ (L_m/n_B) (\Sigma_D^+)^2 \right] \quad (2.67a)$$

The formulation of equilibrium relationships between  $[D]$  and  $[D^+]$  is exactly that of Case (I. 2). The results are represented by Equation (5.66a) for donors on a p-type semiconductor and Equation (5.66b) for acceptors on an n-type semiconductor. The repetition of the equations is therefore omitted.

### The Adion Isotherms - Equilibrium Relationships

#### Between the Gas Phase and Subsystem 4

Having established the equilibrium relationships between subsystems 3 and 4, we shall proceed to formulate the adion isotherms, which are the equilibrium relationships between the gas phase and the adions.

There are two classes of cases as in the last section. Therefore, the division of cases is the same as before.

Case I. Adion Isotherms Associated with Accumulation Space

Charge Regions.

The situations for low surface coverage and moderate-to-high surface coverage must be distinguished as before.

Case (I. 1), Low Coverage of Adions over an Accumulation Layer,  $u_s = 1$ .

The adion isotherms can be obtained by combining Equations (5.58a) and Equation (5.44a). The result is

$$\begin{aligned}
 & [D^+] \left\{ 1 + (L_m/n_B)^{1/2} ([D^+] \pm [F^\pm]) [D^+] \right\} \\
 &= \frac{1}{2} \frac{\beta I_3 r_3}{\sqrt{(n\beta)^{3/2} I_1 kT}} \exp \left\{ (\phi_{n,B} + w_3 - \Delta - \epsilon_d) / kT \right\} (P_{D_n})^{1/n} \quad (5.79a)
 \end{aligned}$$

A special case arises from Equation (5.79a); namely, when  $\Sigma_{\square}^+ = [D^+] - [F^-] = 0$ , then Equation (5.79a) is reduced to the form

$$[D^+] = (\text{constant}) (P_{D_n})^{1/n} \quad (5.80a)$$

An equation of the form of Equation (5.80) has been obtained by Krusemeyer and Thomas<sup>(9)</sup> by a numerical calculation for their localized Langmuir's model of gas adsorption at extremely low total gas coverage so that  $(1 - \theta) \cong 1$ .

The corresponding negative adion isotherm on p-type or intrinsic semiconductor can be written in a similar manner

$$\begin{aligned}
 & [A^-] \left\{ 1 + (L_m/p_B) ([A^-] \pm [F^\mp]) [A^-] \right\} \\
 &= \frac{2\beta I_3 r_3}{\sqrt{(n\beta)^{3/2} I_1 kT}} \exp \left[ (\phi_{p,B} + w_3 - \Delta - \epsilon_A) / kT \right] (P_{A_n})^{1/n} \quad (5.79b)
 \end{aligned}$$

and the special case for  $\Sigma_{\square}^- = 0$ , is

$$[A^-] = (\text{constant}) (P_{A_n})^{1/n} \quad (5.80b)$$

Case (I. 2), High Coverage of Adions over an Accumulation Layer,

$$\underline{u_s > 2.}$$

The adion coverage is such that  $u_s > 2$ , for donors on intrinsic or n-type semiconductor; and  $u'_s > 2$  for acceptors on intrinsic or p-type semiconductor.

Case (I. 2a), Surface Donors or Acceptors on Intrinsic Semiconductor.

The desired relationship can be found by combining Equations (5.65a) and (5.44a) for singly charged donors. The result is

$$[D^+] = (1/C_{i,d})^{1/3} (\beta I_3 r_3 / \sqrt[n]{kT(n\beta)^{3/2} I_1})^{1/3} \exp [(w_3 - \Delta) / 3nkT] (P_{D_n})^{1/3n}$$

Since

$$C_{i,d} = \frac{2L_m}{(N_v N_c)^{1/2}} \exp (\epsilon_d / kT)$$

Therefore

$$[D^+] = \left[ \frac{\sqrt{N_v N_c}}{2L_m} \right]^{1/3} \left[ \frac{\beta I_3 r_3}{\sqrt[n]{kT(n\beta)^{3/2} I_1}} \right]^{1/3} \exp \left[ \frac{w_3 - \Delta - n\epsilon_d}{3nkT} \right] (P_{D_n})^{1/3n} \quad (5.81a)$$

For surface acceptors on an intrinsic semiconductor Equations (5.75b) and (5.44b) can be combined to relate the concentration of singly ionized acceptors to the partial pressure of the acceptor gas.

Since

$$C_{i,A} = \frac{L_m}{(N_v N_c)^{1/2}} \exp (\epsilon_A / kT)$$

Therefore

$$[A^-] = \left[ \frac{2\sqrt{N_V N_C}}{L_m} \right]^{1/3} \left[ \frac{\beta I_3 r_3}{n \sqrt{(n\beta)^{3/2} kT I_1}} \right]^{1/3} \exp \left[ \frac{w_3 - \Delta - n\epsilon_A}{3nkT} \right] (P_{A_n})^{1/3n} \quad (5.81b)$$

Case (I.2b), Donors on n-Type Semiconductor or Acceptors on p-Type Semiconductor.

For donors on an n-type semiconductor, the desired relationship can be obtained by combining Equations (5.66a) and (5.44a); the result is

$$[D^+] = \left[ \frac{N_C}{2L_m} \right]^{1/3} \left[ \frac{\beta I_3 r_3}{n \sqrt{kT(n\beta)^{3/2} I_1}} \right]^{1/3} \exp \left[ \frac{w_3 - \Delta - n\epsilon_d}{3nkT} \right] (P_{D_n})^{1/3n} \quad (5.82a)$$

For acceptors on a p-type semiconductor the result is obtained from Equations (5.66b) and (5.44b).

$$[A^-] = \left[ \frac{2 N_V}{L_m} \right]^{1/3} \left[ \frac{\beta I_3 r_3}{n \sqrt{kT(n\beta)^{3/2} I_1}} \right]^{1/3} \exp \left[ \frac{w_3 - \Delta - n\epsilon_A}{3nkT} \right] (P_{A_n})^{1/3n} \quad (5.82b)$$

Equations (5.82a) and (5.82b) relate the surface ion concentrations to the gas pressure under equilibrium conditions.

Case II. Adion Isotherms Associated with Depletion-Inversion  
Space Charge Regions.

Here again the cases for low, moderate and high coverage must be distinguished.

Case (II. 1), Low Surface Ion Coverage,  $u_s < 1$ .

When there is only a slight depletion of majority carriers, the cases are exactly like Case (I. 1). The result is obtained by combining Equations (5.70a) and (5.44a).

$$\begin{aligned}
 [D^+] & \left\{ 1 + \left[ \frac{2L_m}{n_B + p_B} \right]^{1/2} ([D^+] \pm [F^\pm]) [D^+] \right\} \\
 & = \frac{1}{2} \frac{\beta I_3 r_3}{n \sqrt{(n\beta)^{3/2}} I_1 kT} \exp [(\Phi_{n, B} + w_3 - \Delta - \epsilon_d)/kT] (P_{D_n})^{1/n} \quad (5.83a)
 \end{aligned}$$

Similarly for acceptors on an n-type semiconductor the result is

$$\begin{aligned}
 [A^-] & \left\{ 1 + \left[ \frac{2L_m}{n_B + p_B} \right]^{1/2} ([A^-] \pm [F^\pm]) [A^-] \right\} \\
 & = \frac{2\beta I_3 r_3}{n \sqrt{(n\beta)^{3/2}} I_1 kT} \exp [(\Phi_{p, B} + w - \Delta - \epsilon_A)/kT] (P_{A_n})^{1/n} \quad (5.83b)
 \end{aligned}$$

Under extreme cases when  $|u_s| \ll 1$ , the approximate Equations (5.80a) and (5.80b) are again obtained.

Case (II. 2), Adion Isotherm Associated with a Depletion-Inversion  
Space Charge Region.

For moderate coverage of surface donors on p-type semiconductor, the desired adion isotherm is obtained by combining Equations (5.76a) and (5.44a). Equation (5.44a) can also be written as

$$\ln B_p [D] = \ln \left\{ B_p \beta I_3 r_3 \left[ (n\beta)^{3/2} I_1 kT \right]^{-1/n} \right\} \\ + (w_3 - \Delta)/kT + (1/n) \ln (P_{D_n})$$

By combining this expression with Equations (5.74) and (5.76a) for ionized particles

$$B_p [D^+] + \ln B_p [D^+] \cong (1/n) \ln (P_{D_n}) + \frac{w_3 - \Delta + E_g - \epsilon_d + bkT}{kT} \\ + \ln \left\{ p_B B_p \beta I_3 r_3 / 2N_v \left[ (n\beta)^{3/2} I_1 kT \right]^{1/n} \right\} \quad (5.84a)$$

By combining Equations (5.76b) and (5.44b)

$$B_n [A^-] + \ln B_n [A^-] = (1/n) \ln (P_{A_n}) + \frac{w_3 - \Delta + E_g - \epsilon_d + bkT}{kT} \\ + \ln \left\{ 2 n_B B_n \beta I_3 r_3 / N_c \left[ (n\beta)^{3/2} I_1 kT \right]^{1/n} \right\} \quad (5.84b)$$

To simplify Equations (5.84) we let

$$J_{D,p} = \frac{w_3 - \Delta + E_g - \epsilon_d + bkT}{kT} \\ + \ln \left\{ p_B B_p \beta I_3 r_3 / 2N_v \left[ (n\beta)^{3/2} I_1 kT \right]^{1/n} \right\} \quad (5.85a)$$

$$J_{A,n} = \frac{w_3 - \Delta + E_g - \epsilon_A + bkT}{kT} \\ + \ln \left\{ 2 n_B B_n \beta I_3 r_3 / N_c \left[ (n\beta)^{3/2} I_1 kT \right]^{1/n} \right\} \quad (5.85b)$$

Equation (5.84a) can be written

$$B_p [D^+] + \ln B_p [D^+] \cong J_{D,p} + (1/n) \ln (P_{D_n}) \quad (5.86a)$$

Similarly, for acceptors on an n-type semiconductor

$$B_n [A^-] + \ln B_n [A^-] \cong J_{A,n} + (1/n) \ln (P_{A_n}) \quad (5.86b)$$

Under the condition that

$$B_p [D^+] \gg \ln B_p [D^+] \text{ or } B_n [A^-] \gg \ln B_n [A^-]$$

Then Equation (5.86a) becomes

$$B_p [D^+] \approx J_{D,p} + (1/n) \ln (P_{D_n}) \quad (5.87a)$$

and Equation (5.86b) becomes

$$B_n [A^-] = J_{A,n} + (1/n) \ln (P_{A_n}) \quad (5.87b)$$

Case (II. 3), Adion Isotherm Associated with a Strong Inversion  
Space Charge Region.

The isotherms for this situation are exactly like those of Equations (5.82a) and (5.82b). This similarity was also indicated under the discussion for Case (II. 3) in the previous section.

SUMMARY OF EQUATIONS

For the convenience of discussion and representation we shall simplify and summarize all of the previously derived isotherms for neutral and charged ad-particles. The following coefficients can be defined.

$$K_m = \left( \frac{I_2 r_2}{I_1} \right) \left[ \frac{1}{(n\beta) (kT)^2} \right]^{1/2} \exp (w_2/kT) \quad (5.88)$$

$$K_a = \frac{\beta I_3 r_3}{n \sqrt{(n\beta)^{3/2} kT I_1}} \exp \left[ \frac{w_3 - \Delta}{kT} \right] \quad (5.89)$$

$$C_i = \left[ \frac{\sqrt{N_v N_c}}{2L_m} \frac{(\beta I_3 r_3)}{n \sqrt{(n\beta)^{3/2} I_1 kT}} \right]^{1/3} \exp \left[ \frac{w_3 - \Delta - n\epsilon_d}{3nkT} \right] \quad (5.90a)$$

$$C_e = \left[ \frac{N_c}{2L_m} \frac{(\beta I_3 r_3)}{\sqrt[n]{(n\beta)^{3/2} I_1 kT}} \right]^{1/3} \exp \left[ \frac{w_3 - \Delta - n\epsilon_d}{3nkT} \right] \quad (5.91a)$$

$$K_i = \left[ \frac{2\sqrt{N_v N_c}}{L_m} \frac{(\beta I_3 r_3)}{\sqrt[n]{(n\beta)^{3/2} I_1 kT}} \right]^{1/3} \exp \left[ \frac{w_3 - \Delta - n\epsilon_A}{3nkT} \right] \quad (5.90b)$$

$$K_e = \left[ \frac{2N_v}{L_m} \frac{(\beta I_3 r_3)}{\sqrt[n]{(n\beta)^{3/2} I_1 kT}} \right]^{1/3} \exp \left[ \frac{w_3 - \Delta - n\epsilon_A}{3nkT} \right] \quad (5.91b)$$

With the above defined coefficients, the adsorption isotherms of neutral and charged particles are now summarized.

#### Adsorption Isotherms of Neutral Particles

For adsorbed molecules

$$[D_n] = K_m (P_{D_n}) \quad (5.38a')$$

$$[A_n] = K_m (P_{A_n}) \quad (5.38b')$$

For adsorbed atoms

$$[D] = K_a (P_{D_n})^{1/n} \quad (5.44a')$$

$$[A] = K_a (P_{A_n})^{1/n} \quad (5.44b')$$

#### Adsorption Isotherms of Charged Ad-Particles

For very low adion concentration  $|u_s| \ll 1$ .

$$[D^+] = (\text{constant}) (P_{D_n})^{1/n} \quad (5.80a')-(5.83a')$$

$$[A^-] = (\text{constant}) (P_{A_n})^{1/n} \quad (5.80b')-(5.83b')$$



For high adion coverage  $|u_s| > 2$ .

For adions on an intrinsic semiconductor

$$[D^+] = C_i (P_{D_n})^{1/3n} \quad (5.81a')$$

$$[A^-] = K_i (P_{A_n})^{1/3n} \quad (5.81b')$$

For adions on extrinsic semiconductors; adsorption associated with accumulation space charge region, donors on an n-type semiconductor

$$[D^+] = C_e (P_{D_n})^{1/3n} \quad (5.82a')$$

For acceptors on a p-type semiconductor

$$[A^-] = K_e (P_{A_n})^{1/3n} \quad (5.82b')$$

For adsorption associated with depletion-inversion space charge region, donors on a p-type semiconductor

$$B_p [D^+] + \ln B_p [D^+] \cong J_{D,p} + (1/n) \ln (P_{D_n}) \quad (5.86a)$$

For acceptors on an n-type semiconductor

$$B_n [A^-] + \ln B_n [A^-] \cong J_{A,n} + (1/n) \ln (P_{A_n}) \quad (5.86b)$$

Under conditions that

$$B_p [D^+] \gg \ln B_p [D^+]$$

$$B_n [A^-] \gg \ln B_n [A^-]$$

then, for donors on a p-type semiconductor

$$B_p [D^+] \cong J_{D,p} + (1/n) \ln (P_{D_n}) \quad (5.87a)$$

and for acceptors on an n-type semiconductor

$$B_n [A^-] \cong J_{A,n} + (1/n) \ln (P_{A_n}) \quad (5.87b)$$

For non-dissociative charge transfer adsorption, there are only two kinds of ad-particles in the adsorbed phase, neutral molecules and ionized molecules. The corresponding equations can be easily obtained by using the following replacements:

n	becomes	1
$\Delta$	becomes	0
$w_3$	becomes	$w_2$
$I_3 r_3$	becomes	$I_2 r_2$

### DISCUSSION

In the following discussion, we shall first point out the special features of the formulated adsorption isotherms. These features are:

(i) Adsorption isotherms for each adsorbed species are given separately.

(ii) The adsorption isotherms for neutral particles are of Freundlich's type adsorption isotherms.

(iii) The adsorption isotherms for charged particles are dependent on the space charge region generated upon adsorption; namely, a Freundlich type adsorption isotherm is associated with an accumulation space charge region, or a strongly inverted space charge region; a logarithmic type adsorption isotherm is associated with depletion-inversion space charge region.

Naturally, the total gas uptake,  $\theta$ , is the summation of all the adsorbed species on the semiconductor surface. For example, the total donor gas,  $D_n$ , adsorbed on a n-type semiconductor producing an accumulation layer with  $u_s \geq 2$ , is given by

$$\theta = [D_n] + [D] + [D^+] \approx K_m (P_{D_n}) + K_a (P_{D_n})^{1/n} + C_e (P_{D_n})^{1/3n} \quad (5.88)$$

That is,  $\theta$  is expressed by a polynomial function of pressure instead of a single term as in the Freundlich type adsorption isotherm.

The sample Equation (5.88) shows that if the Freundlich equation is approximated

$$\theta = \text{const.} (P_{D_n})^{1/\gamma} \quad (5.88a)$$

then  $\gamma$  must be

$$1 \leq \gamma \leq 3n \quad (5.89)$$

For the case of a donor gas on a p-type semiconductor when a depletion-inversion space charge region is generated,  $\theta$  can be expressed by the following equation for an extreme case

$$\theta \approx K_m (P_{D_n}) + K_a (P_{D_n})^{1/n} + \frac{1}{nB_p} \ln (P_{D_n}) + J_{D,p}/B_p \quad (5.90)$$

for  $(P_{D_n}) \neq 0$ . In case of Equation (5.90) the Freundlich empirical correlation may require an even larger  $\gamma$ . From the above sample Equations (5.88) and (5.90), it is further seen that to check the adsorption isotherm by measuring the total amount gas uptake,  $\theta$ , against pressure is rather difficult and indecisive. However, if one sets out to check the adsorption isotherm for charged particles, the situation is completely different. For example,  $[D^+]$  or  $[A^-]$  will affect the work function,  $\Phi_{th}$ , and the surface conductance,  $\Delta\sigma_s$ , which have been derived in Chapters 3 and 4. For example, in case of high surface ion concentration  $[A^-]$  on p-type (or  $[D^+]$  on n-type) semiconductor, it was shown in Chapter 3 that

$$\Delta\sigma_s = q\mu_p [A^-] \quad (3.23)$$

Since  $[A^-]$  is related to the partial pressure of  $A_n$  through Equation (5.82b'), the combination of these two equations gives

$$\Delta\sigma_s = K_e q\mu_p (P_{A_n})^{1/3n} \quad (5.91)$$

In case of nondissociative molecular ions,

$$\Delta\sigma_s = \text{const.} (P_{A_n})^{1/3} \quad (5.91a)$$

Similarly in the case of the work function as function of pressure, we can use the derived relationships in Chapter 4. For example, Equation (4.48)

$$\Delta\phi_{th} \cong -kT \ln \left\{ (L_m/n_B) [D^+]^2 \right\} + \text{const.} \quad (4.48)$$

can be expressed in terms of pressure by using Equation (5.82a), (donors on n-type); the result is

$$\Delta\phi_{th} \cong -\frac{2kT}{3n} \ln (P_{D_n}) + \text{const.} \quad (5.92)$$

For nondissociative adsorption, the result is

$$\Delta\phi_{th} = -\frac{2kT}{3} \ln (P_{D_n}) + \text{const.} \quad (5.92a)$$

In the following section the derived isotherms and relationships deduced from them, such as Equations (5.91) and (5.92) will be compared with experimental observations in literature.

### Comparison with Experimental Observations

In this section, we shall present reported observations on the adsorption of gases or vapors on semiconductor surfaces which may involve charge transfer.

We shall discuss the adsorption of hydrogen on germanium. Tamaru<sup>(23)</sup> has studied the adsorption of hydrogen on a clean germanium film prepared by decomposition of germane on glass wool. The temperature of his experiment ranges from 218°C to 348°C. He found that the Freundlich isotherm is applicable except at lower pressures. The value of  $\gamma$  in Equation (5.88a) ranges from 5 to 1.85. He further reported that the adsorption is dissociative. From Equation (5.89),  $\gamma$  should be

$$1 \leq \gamma \leq 6 \quad (5.90a)$$

Therefore Tamaru's observation is in our range of prediction. Since this is a wide range, we cannot put too much emphasis on the adsorption data as we have pointed out in a previous section.

We shall now discuss variations in the work function or contact potential as a function of vapor pressure.

Roginsky<sup>(24)</sup> reported a graphical relation between the work function variation,  $\Delta\phi_{th}$ , of an n-type germanium and the pressure of isopropyl alcohol (donor) replotted in Figure 5.5. He did not report the temperature under which the data were taken nor the units of pressure. Therefore we cannot estimate the slope of the  $\Delta\phi_{th}$  vs.  $\log P$  plot. Nevertheless Equation (5.92) or Equation (5.92a) is borne out from this linear plot of  $\Delta\phi_{th}$  vs.  $\log P$ .

Liashenko and Litovchenko<sup>(25)</sup> reported that when acetone (donor) was adsorbed on an n-type germanium surface, the work function,  $\Delta\phi_{th}$ , of germanium is decreased. They presented their data by plotting  $\Delta\phi_{th}$  against the square root of the pressure of acetone in Figure 5.6. Two sets of their data with  $|\Delta\phi_{th}| > 2kT$  are replotted in Figure 5.7 as  $-\Delta\phi_{th}$  vs.  $\log P$ . Again the linear relationship between  $-\Delta\phi_{th}$  and  $\log P$  is verified. The calculated slopes are 0.88 and 0.51 which are close to the value of 0.67 predicted by Equation (5.92a). It also indicates that acetone was adsorbed as positive molecular ions (a donor) on n-type germanium.

## CONCLUSION

Adsorption isotherms of neutral and charged ad-particles based on a generalized mobile adsorption model have been formulated. The special features of these adsorption isotherms have been discussed and compared with published data on gas adsorption and work function variations. The general predictions of adion isotherm have been borne out by the observation of adsorption isotherms and of work function variations as functions of gas pressure.

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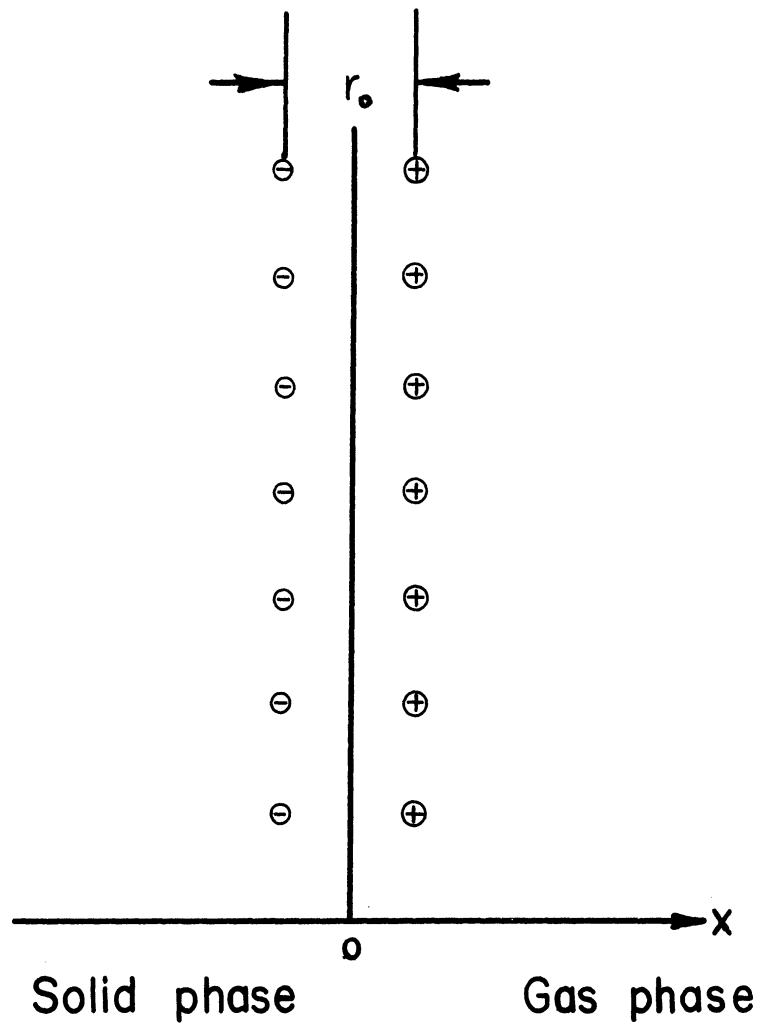


Figure 5. 1.

Model for semiconductor surface with very low adion concentration showing formation of dipoles between the adions and the image charges.

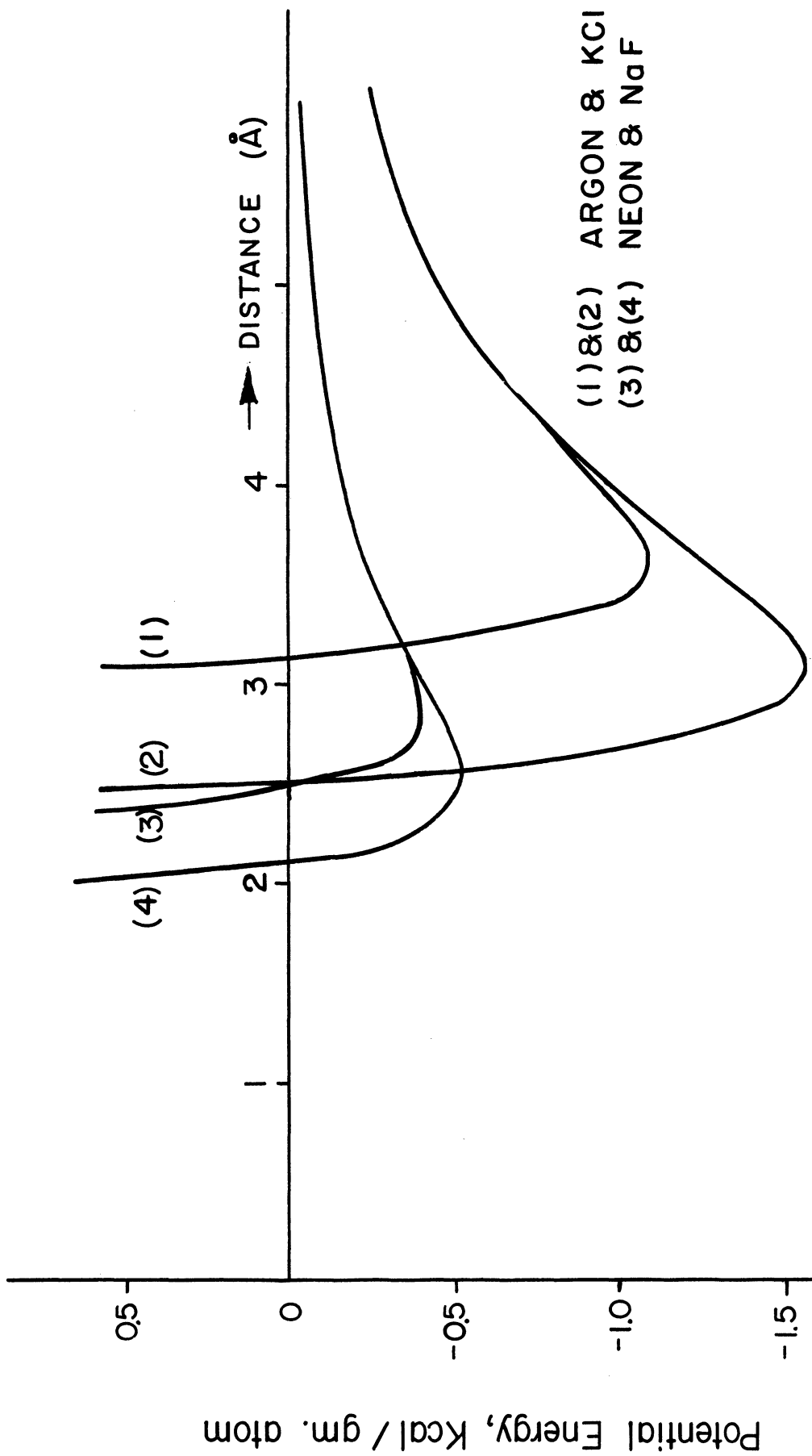


Figure 5.2. The potential energy of an argon atom outside a (100) plane of a KCl crystal (1) above a lattice point, (2) above the midpoint of a lattice cell. (The lattice constant  $a = 6.28 \text{ \AA}$ ). Curves 3 and 4 are similar results for neon above NaF crystal. ( $a = 4.68$ ).

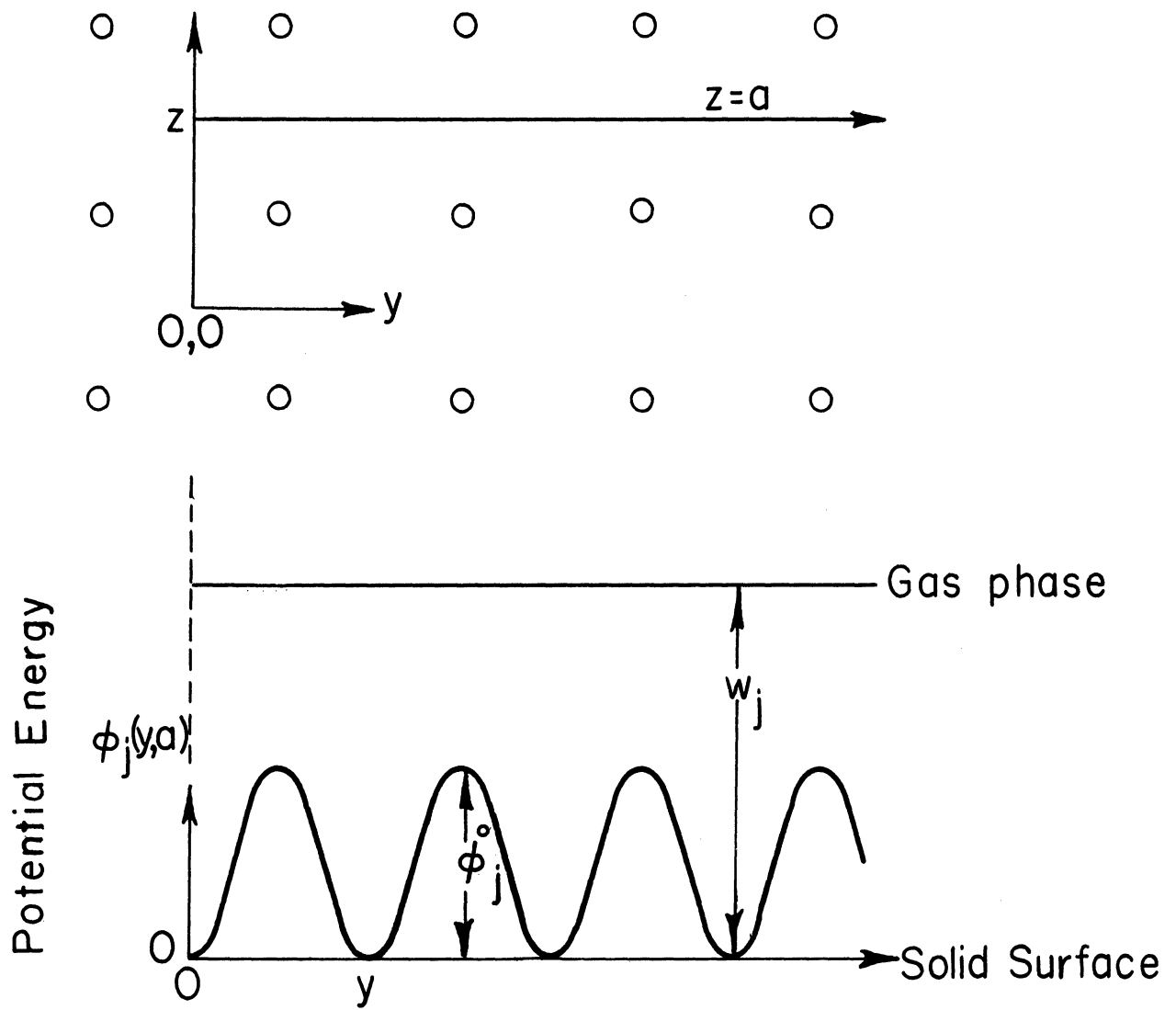


Figure 5.3. Illustration of surface migration restricting potential energy and energy of desorption or adsorption.

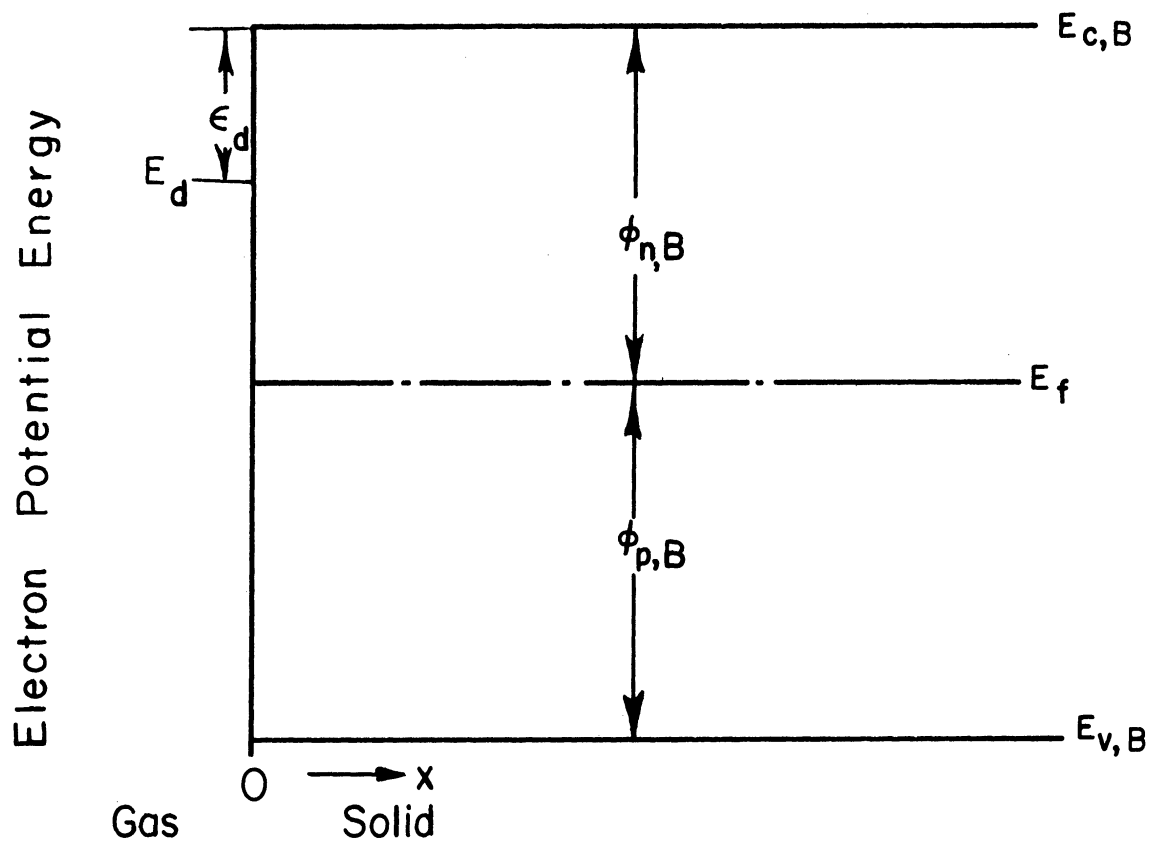


Figure 5.4 a. Initial condition when donor is about starting to become ionized.

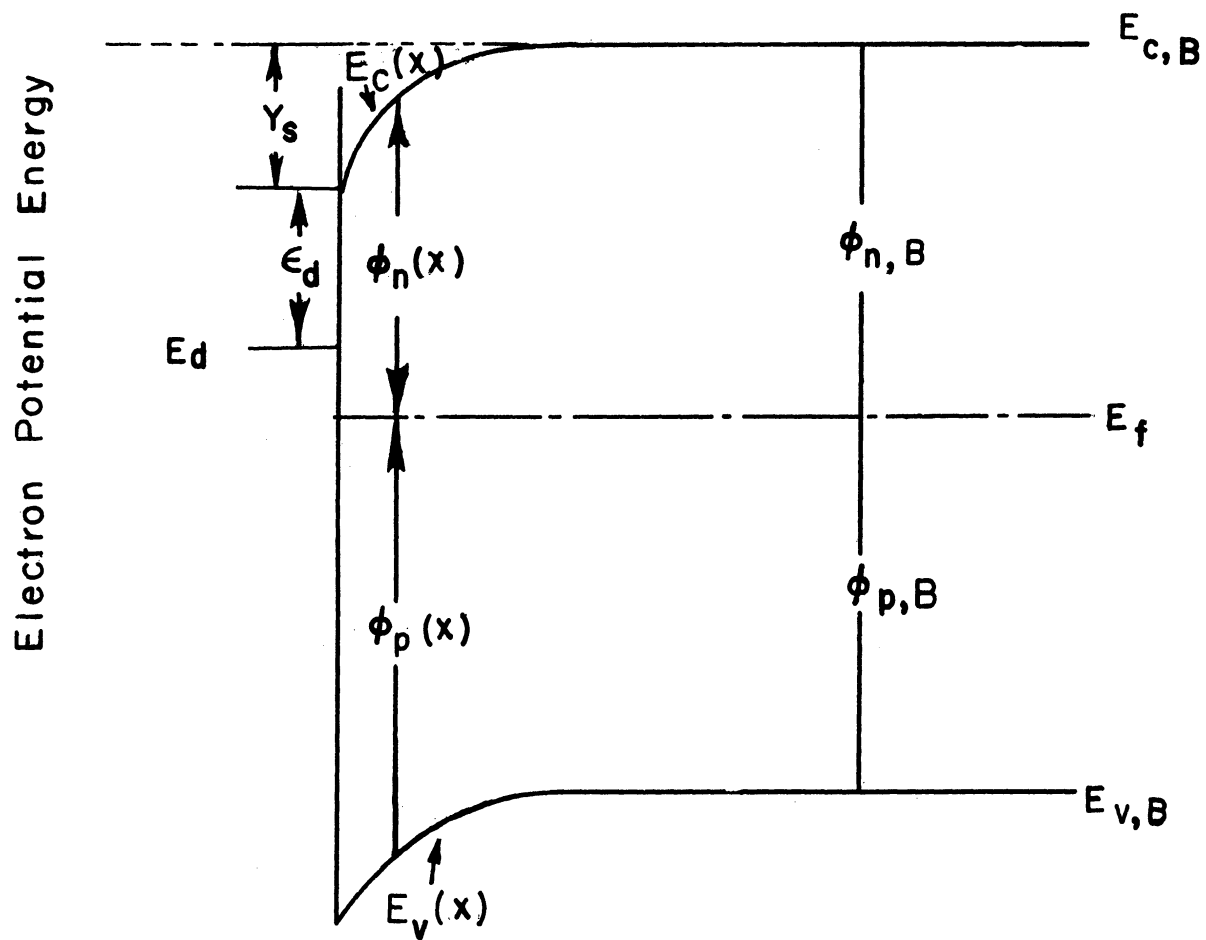


Figure 5.4 b.

Customary energy band diagram for adsorption of donors in progress.

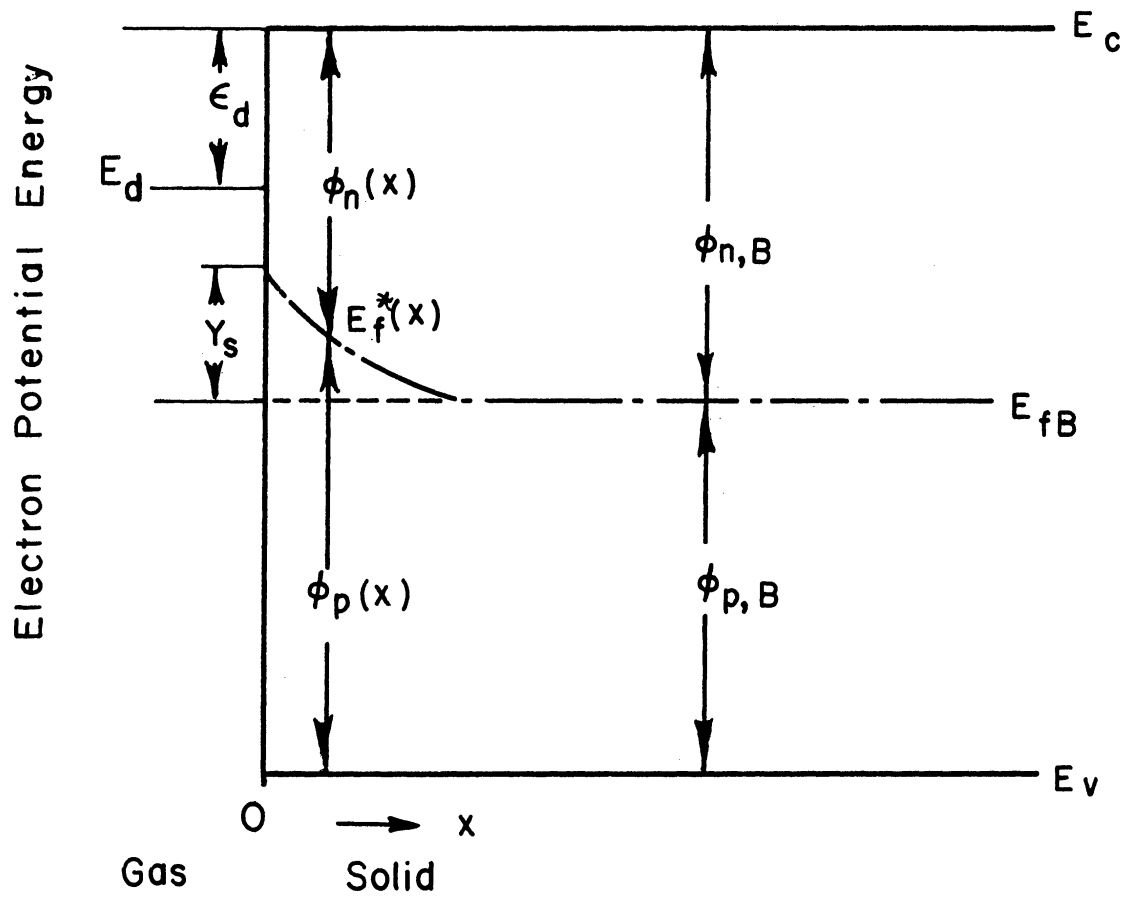


Figure 5.4 c.

Energy band diagram as proposed in Chapter 4 for the adsorption of donors.

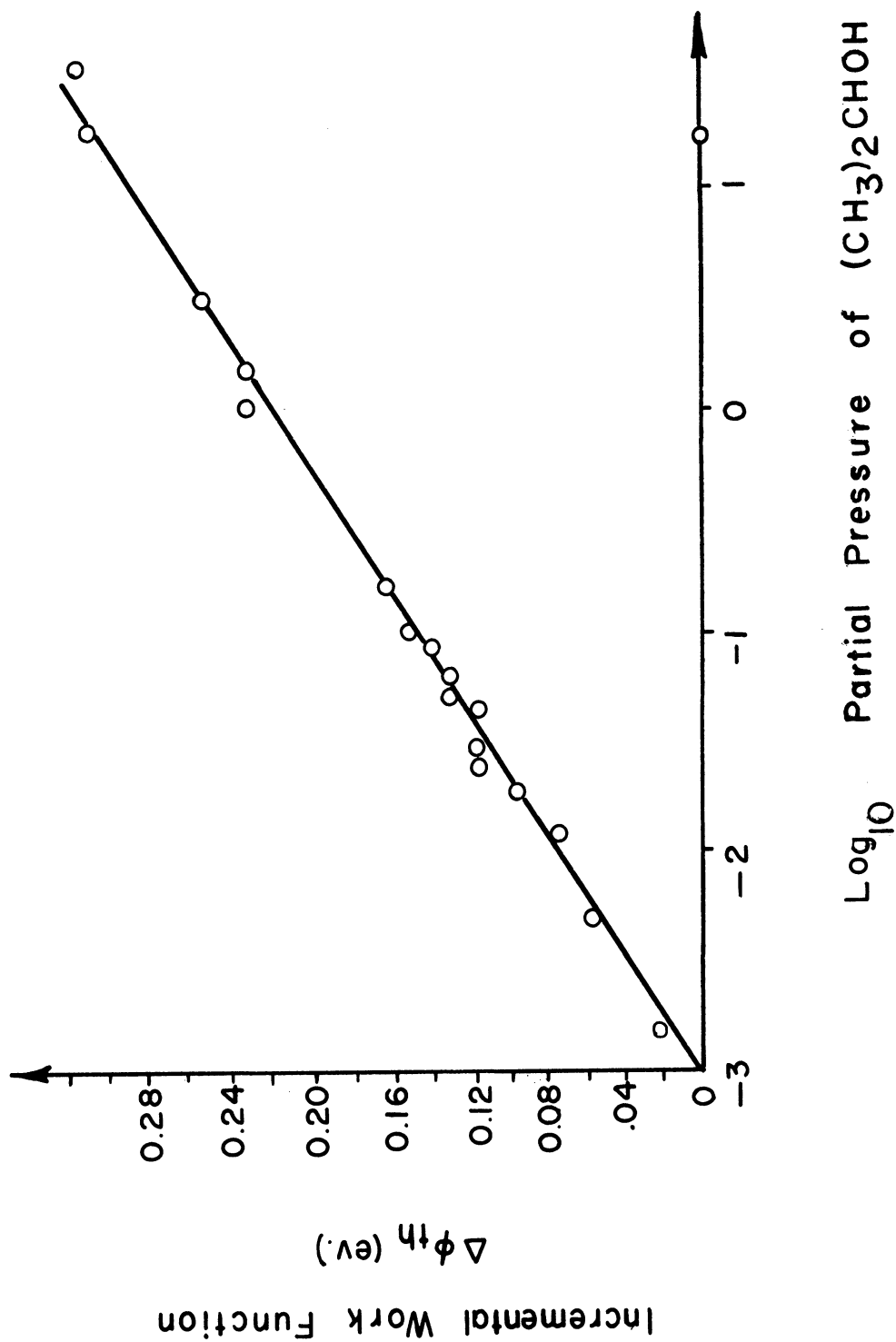


Figure 5.5. Variation of work function,  $\Phi_{th}$ , of n-type Ge vs. the pressure of isopropyl-alcohol.

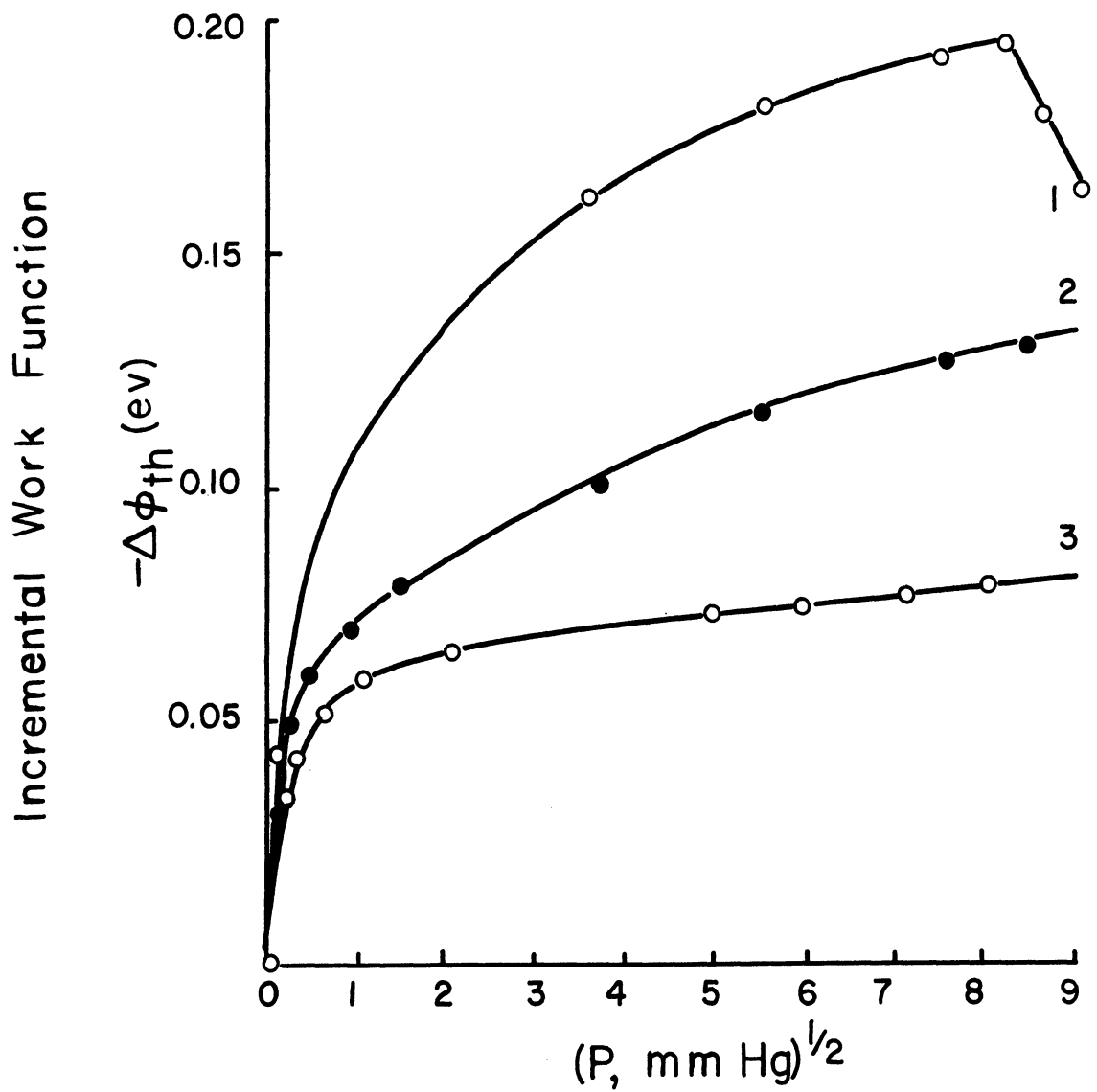


Figure 5.6.

Dependence of the change of work function,  $\Delta\phi_{th}$ , on the gas phase pressure of acetone which is adsorbed on n-type germanium. The curves were obtained for the following temperatures: (1) 16°C, (2) 85°C, (3) 165°C.



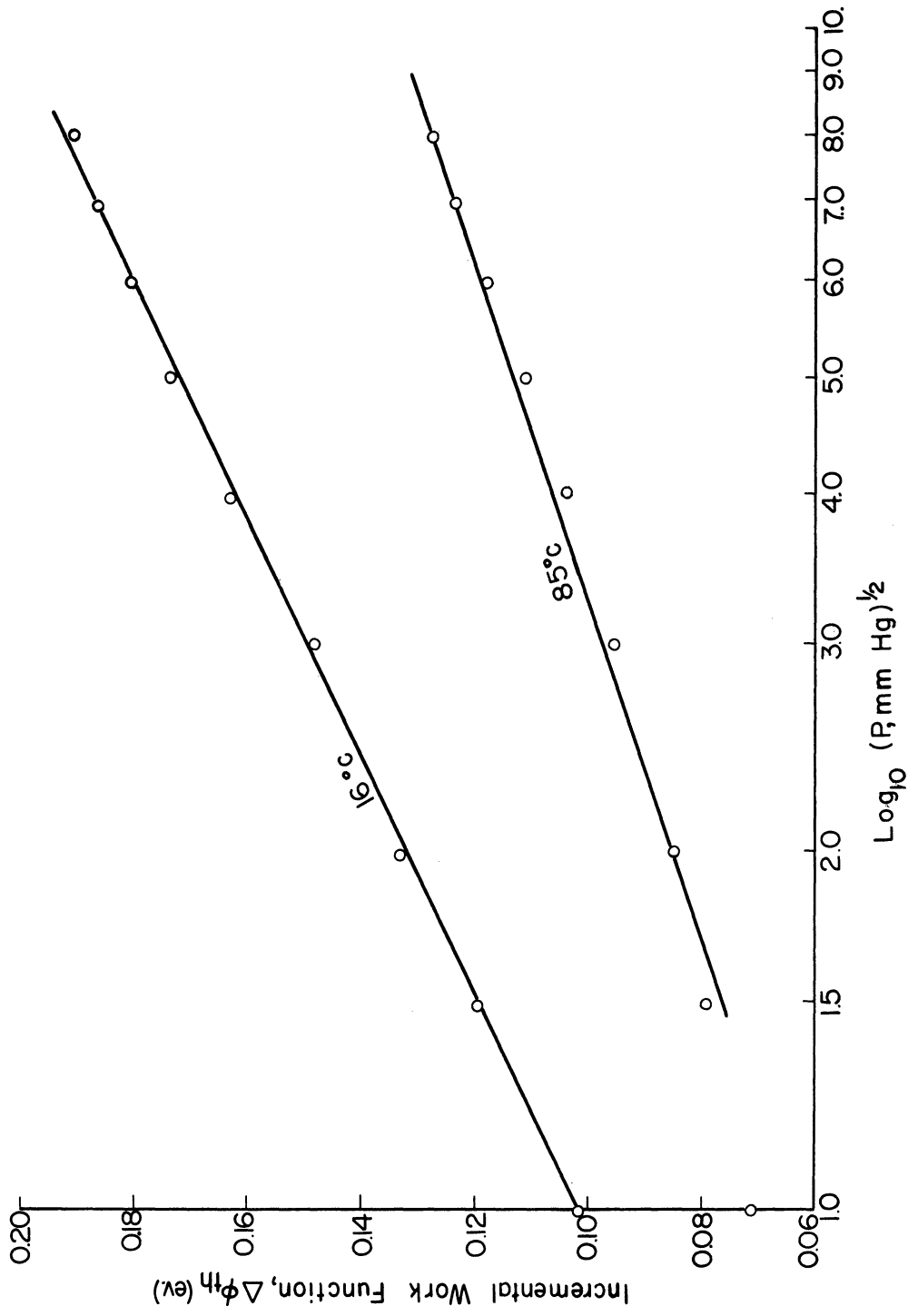


Figure 5.7.

Dependence of the change of work function,

$\Delta\phi_{th}$ , on the gas phase pressure of acetone

which is adsorbed on n-type germanium. The

curves were obtained by replotting the data

represented in Figure 5.6 for temperatures

(1) 16°C and (2) 85°C.

