KINETIC THEORY OF ADSORPTION AND DESORPTION OF GASES ON SEMICONDUCTOR SURFACES

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ABSTRACT

In this report the rate equations for adsorption and desorption of gases are derived on the basis of a charge transfer model. The rate equations for adsorption on different types of semiconductors are compared with data from the literature. The observed changes in electrical conductivity and work function during adsorption are also explained quantitatively.

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CHAPTER 6

KINETIC THEORY OF ADSORPTION AND DESORPTION OF GASES ON SEMICONDUCTOR SURFACES

INTRODUCTION

The rate processes of adsorption and/or desorption of gases or solids have been studied by both chemists and chemical engineers for over three decades(1) as a means towards the understanding of heterogeneous catalytic chemical reactions. With the advent of semiconductor technology, a new field of research, namely the semiconductor surfaces, was brought in with new vitality and new tools of experimentation. This latter research not only has provided a good quantitative understanding of the electrical properties of semiconductor surfaces, but also has established the gas-surface interaction via "charge transfer adsorption," which generates a space charge region, (S. C. R.), in the semiconductor.

The simultaneous measurements of the rate of variation of some electrical properties of a semiconductor surface, (e.g. the work function or surface conductivity), and the rate of gas adsorption have provided new insights to the understanding of the rate of adsorption on semiconductor surfaces. Although the "charge transfer" hypothesis for adsorption and/or desorption of gases on semiconductors has long been postulated and considered by many authors,(1-6) a quantitative check which permits the direct association between the rate of change of electric properties of semiconductor and that of gas adsorption has been lacking until recently. At the 1960 Prague Conference of Semiconductor Physics, Enikeev, Roginsky and Rufov(7) reported detailed measurements on the rate of change of work function, $\Delta\phi_{th}$, and the rate of gas adsorption, which can be summarized in the following statements.

For accumulation adsorption, i.e., an accumulation S. C. R. is created during adsorption; e.g. oxygen (acceptor) on NiO (p-type semiconductor):

$$\Delta\phi_{th} \propto \log t \tag{6.1}$$

$$\Delta\theta \propto t^{1/m} \tag{6.2}$$

$$\Delta\phi_{th} \propto \log \Delta\theta \tag{6.3}$$

For depletion adsorption, i.e., a depletion S. C. R. is created during adsorption, e.g. oxygen (acceptor) on ZnO (n-type), or MnO_2 (n-type).

$$\Delta\phi_{th} \propto \log t \tag{6.4}$$

$$\Delta\theta \propto \log t \tag{6.5}$$

$$\Delta\phi_{th} \propto \Delta\theta \tag{6.6}$$

where "t" is time, $\Delta\theta = \theta - \theta_o$, θ_o is the initial gas up-take which is dependent on the preparational procedure. These observations agree with those of Barry and Stone,(8) Linde,(9) Sebenne(10) and Melnick,(11) who present both adsorption and electrical measurements, but contradicts those of Engell and Hauffe,(2) whose data contains only adsorption measurements without substantiating electrical measurements.

The results presented by Enikeev et al are in complete accord with our conclusions reached in Chapter 4, that the space charge region adjacent to gas-solid phase boundary dominates the gas-surface interactions on semiconductors. At the same time these results can not be explained by the heterogeneous surface model,(12) the site generation or annihilation models(13-15) or the simple dipole layer model.(16) None of these theories predict or even assume that the rate laws of gas adsorption are associated with the space charge region or the typeness of the semiconductor catalyst upon which the adsorption process occurs! However, in addition to the affirmation of the charge transfer theory of chemisorption and catalysis, all these experimental results further indicate the inadequacy of the present-day "charge transfer" adsorption theories. For example, equations (6.1), (6.2), (6.4) and (6.5)(17) have never been satisfactorily derived nor completely understood on a monolithic basis of the charge transfer theory gas-surface interactions and heterogeneous catalysis on semiconductors.

In this chapter, we shall formulate the rate laws for adsorption and desorption of charged particles. The related rate of change of electric properties of the semiconductor surface will be discussed.

LITERATURE SURVEY

Rate "laws" for adsorption and desorption of gases on solid surfaces have been critically reviewed by Low(1) in 1960. These rate "laws", or more correctly, rate expressions, resulted from either theoretical considerations or experimental observations. It is seen from these reviews that theoretical works devoted to the explanation of adsorption kinetics far outbalance those devoted to desorption kinetics.

For adsorption, two kinds of empirical rate laws are observed, namely, the power rate law, $\theta \propto t^{1/m}$ (18) and the logarithmic rate law, $\theta \propto \log(t + t_o)$.(19) So far there is no theory which can provide a monolithic explanation for both of these observations.

In recent years, the logarithmic rate law has been in the limelight. Many theoretical models(1) have been proposed for its explanation. Perhaps never before have so many people explained so little. Thus, Low(1) wrote, "It suffices for the present purposes to state that none of the models appears to be satisfactory.... As a consequence of this, the use of a particular chemisorption mechanism is almost a matter of personal preference until much more experimental and theoretical work has been done and an adequate model emerges."

Among the models which are pertinent to the adsorption and/or desorption of charged particles are the "charge transfer models" of chemisorption.(2-6, 8, 11) The general development of this charge transfer theory of chemisorption and catalysis on semiconductors has been reviewed in Chapter 5. Several of these authors have considered the kinetics of adsorption of charged particles (molecular ions or atomic ions). We shall review these theoretical rate laws for the adsorption of ions, or adsorption processes which include ions in one of the critical steps.

Engell and Hauffe(2, 3) have postulated that "the rate-determining step is the electron transfer between the adsorbent and the adsorbate, the work function will be increased with increasing coverage of the surface, since the energy barrier, to be overcome by the electrons moving from the solids to the adsorbate, will be increased with increasing coverage of the surface." With this assumption, a rate equation equivalent to the following is obtained,

$$\frac{d[A^-]}{dt} = K_H \exp\left\{-q(U_H - \Delta\phi_H)/kT\right\} \tag{6.7}$$

where qU_H is the height of the energy barrier at the beginning of chemisorption ($[A^-] = 0$), and $q\Delta\phi_H$ is the "difference between the work functions for a free surface and one occupied by adsorbed particles." The pre-exponential factor, K_H, is "the frequency factor of the chemisorption," which is proportional to the fraction of electrons that are in a state of transition from a lower to a higher energy level, which was assumed by Engell and Hauffe to be constant "at least for the start of chemisorption".

With the above mentioned postulates, Engell and Hauffe derived a rate law for the adsorption of oxygen on nickel oxide, NiO. Engell and Hauffe evaluated $\Delta\phi_H$ by solving Poisson's equation in one-dimensional form for an accumulation space charge region; i.e., oxygen (acceptor) on NiO (p-type semiconductor). However, due to their mathematical difficulties, they did not obtain an explicit function of the diffusion potential, V_D, in terms of surface charge. Their V_D can be shown to be Y_s/q in the notation we have been using from Chapter 2. In addition to the diffusion potential, they further assumed that there was a dipole layer on the semiconductor, NiO. They gave $\Delta\phi_H$ in the following equivalent form:

$$\Delta\phi_H = -a_H \frac{4\pi q}{\epsilon}[A^-] - V_D \tag{6.8}$$

where a_H = constant. The diffusion potential was expressed as

$$V_D = \frac{kT}{q} \ln\left\{\frac{2\pi q}{\epsilon} \frac{[A^-]^2}{(p_B)} \frac{1}{V_D}\right\} \qquad (6.9)$$

It is clear that they did not obtain an explicit function for V_D. Equation (6.8), as presented in reference (2) as Equation (11), is correct; the same equation was presented in reference (3) as Equation (31), but the negative sign before the first term was missing.

By substitution of Equation (6.8) into Equation (6.7), they obtained the following equation, (again in equivalent form).

$$\frac{d[A^-]}{dt} = K_H (\epsilon\, p_B V_D / 2\pi\, q)\, (1/[A^-]^2)$$

$$\exp\left\{- (U_H q \epsilon + 4\pi q^2 a_H [A^-])/\epsilon kT\right\} \qquad (6.10)$$

Equation (6.10) is the correct form of Equation (33) in reference (3), where the plus sign in the exponential term $(U_H q\epsilon + 4\pi q^2 a_H [A^-])$ is missing.

It is obvious that with Equation (6.10), they could not obtain the logarithmic rate law of chemisorption, which they claimed without justification, that V_D in Equation (6.10) could be replaced by a constant. Granting that this could be done, Equation (6.10) can be reduced to the following form:

$$\frac{d[A^-]}{dt} = (\alpha_H / [A^-]^2)\ \exp(- \beta_E [A^-]) \qquad (6.10a)$$

where, $\alpha_H = K_H(\epsilon\, p_B V_D / 2\pi\, q)\ \exp(- U_H q/kT)$

$$\beta_E = 4\pi q^2 a_H / \epsilon kT \qquad (6.10b)$$

Although Equation (6.10a) can be integrated, Engell and Hauffe have not shown the results of this integration. The present author has performed the integration, the result of which is:

$$\left\{\beta_E^2 [A^-]^2 - 2\beta_E [A^-] + 2\right\} \exp\left\{\beta_E [A^-]\right\} = \alpha_H \beta_E^3 t + 2 \qquad (6.11)$$

Only under the condition that,

$$2 >> \beta_E^{\,2}\,[A^-]^2 - 2\beta_E\,[A^-]$$

that is, when $[A^-]$ approaches zero, then Equation (6.11) reduces to the logarithmic rate expression which was presented by Engell and Hauffe without the qualification that $[A^-]$ must be small. Therefore

$$[A^-] = (1/\beta_E)\ \ln[\,\alpha_H\,\beta_E^{\,3}\ t/2 + 1] \qquad (6.13)$$

Equation (6.13) could have been derived without even considering the accumulation space charge region. This can be done by assuming that the rate-limiting step is the charge transfer across the surface dipole layer. Indeed this was assumed indirectly by Engell and Hauffe when they stated that the β_E term in the exponential part in Equation (6.10a) above dominates the relation between the rate of adsorption and surface concentration, $[A^-]$. In their original statement, "Die exponentiellen Glieder werden auch hier wieder den überwiegenden Einfluss auf die Beziehung zwischen Reaktionsgeschwindigkeit und Oberflächenkonzentration." In regard to the surface dipole layer model, it has also been considered by Higuchi, Ree and Eyring(16) within the framework of the transient state rate theory.

In view of the recent data(7-10) and the experimental evidences in Chapters 4 and 5, it is clear that the space charge region in a semiconductor generated by surface charges, the adions, is a dominating factor in the phenomenon of gas-surface interaction on semiconductors. However, for metals or at the initial stage of charge transfer adsorption on semiconductors, the surface dipole layer may be rate-limiting.

Weisz(4) has discussed the adsorption of negative adions, A^-(ads), on n-type semiconductors. He expressed the rate of electron transfer from the n-type semiconductor to surface acceptors by means of the following equation, (again in equivalent form):

$$\frac{d[A^-]}{dt} = C_W\ \exp\left\{-(\phi_{n,B} + Y'_s)/kT\right\} \qquad (6.14)$$

where Y'_s is surface potential in our notation, C_W is a constant, "the frequency factor including the electron concentration and mobility" as assumed by Weisz. He then expressed Y'_s in terms of A^- by the relationship,

$$Y'_s = C'_W [A^-]^2 \tag{6.15}$$

Equation (6.15) represents a special case relating surface potential as a function of the surface charges, which has been pointed out in Chapter 2.

By combining Equations (6.14) and (6.15), the rate of adsorption of $[A^-]$ on an n-type semiconductor is:

$$\frac{d[A^-]}{dt} = C_W \exp\left\{- (\phi_{n,B} + C'_W [A^-]^2)/kT\right\} \tag{6.16}$$

In deriving the equivalent of Equation (6.16) Weisz assumed that the rate-limiting step in the adsorption of adions is the "charge transfer across the space charge region".

In contrast to Engell and Hauffe, Weisz did not assume the presence of a surface dipole layer. Equation (6.16) was not integrated. As a matter of fact, it was Germain(5) who wrote Equation (6.16) by using Weisz's original rate equation for electron transfer.

Assumptions similar to those of Weisz, which lead to Equation (6.16), have been made by Morrison.(6). Later, Melnick(11) applied Equations (6.14) and (6.15), but not Equation (6.16) in his effort to obtain a logarithmic rate law to explain his observations.

Barry and Stone(8) have investigated the adsorption of oxygen on zinc oxide. Their postulates were described by the schematic diagram, Figure 10 of their paper, and stated the following:

"...at zero coverage there is an activation energy, η_B, for adsorption and a heat of adsorption $(\alpha_B - \phi_{o,B})$. As adsorption progresses, each adsorbed particle acquiring one electron, a potential barrier develops due to the depletion of electrons from a layer of the semiconductor adjacent to the surface, increasing the activation energy to $(\eta_B + V_B)$ and decreasing the heat of adsorption to $(\alpha_B - \phi_{o,B} - V_B)$...."

They gave the rate of adsorption for low surface concentration by means of the following equation

$$\frac{d[O^-]}{dt} = A_B \exp\left\{-q(\eta_B + V_B)/kT\right\} \tag{6.17}$$

where A_B = constant

$$V_B = [O^-]\left(\frac{2\pi kT}{\epsilon n_B}\right)^{1/2} \tag{6.18}$$

"V_B" was obtained by solving the one-dimensional Poisson-Boltzmann equation for low surface ion concentration, i.e., $qV_B/kT < 1$. Except for a factor of $\sqrt{2}$, Equation (6.18) was rewritten in the following form,

$$\frac{d[O^-]}{dt} = A'_B \exp\left\{(-B_s[O^-])\right\} \tag{6.19}$$

Equation (6.19) was discussed by saying: "it is interesting to note that this is formally identical with the Roginsky-Zeldovich equation which we found to be accurately obeyed for the rate of depletive chemisorption on ZnO_1," where ZnO_1 is a sample of zinc oxide which has the lowest excess Zn atom concentration, according to the authors.

In view of the above derivations and assumptions, Barry and Stone's model is similar to that of Weisz, except for the low surface ion concentration restriction.

More comprehensively, Garrett(20) has made use of the Hall-Shockley-Read(22-24) model for trapping of carriers in a semiconductor to write down the rate of charge transfer between the adsorbate and the semiconductor. The adsorbed particles, donor or acceptor, are treated as surface "impurity centers" or "trapping centers". This approach is consistent with the Krusemeyer-Thomas paper(38) on charge-transfer adsorption, which has been discussed in Chapter 5. However, Garrett did not apply the rate equations of charge transfer to formulate the rate equations for adsorption and desorption of charged particles, even though such an approach is perhaps more logical than using it to treat unimolecular reactions directly, as was done in his paper.

Garrett has also discussed the location of the donor or acceptor energy level. He pointed out that "the potential energy of the atom, in its neutral and in its ionized state, will be grossly affected by the proximity of the surface". The Auger electron emission was cited by him as qualitative evidence.

However, such a "proximity effect" of a solid surface can be equally understood by considering that the dielectric constant in the proximity of the solid surface might be increased. Consequently the ionization energy or electron affinity of an adsorbed atom will be changed accordingly.(21)

From this brief survey, it is seen that a comprehensive treatment of the kinetics of adsorption and desorption of charged particles is still lacking. For the rate of charge transfer adsorption or unimolecular reactions, the aforementioned works have the following points in common:

I. Charge transfer between the adsorbate and the solid adsorbent, a semiconductor, is always assumed to be the rate-limiting step in adsorption and/or desorption of gases.

II. The charge transfer process is activated, like that of thermionic emission of electrons. The wave mechanical tunneling process was not postulated.

III. Poisson's equation in one-dimensional form has always been applied to obtain the surface potential for a few special cases. The surface potential acts either as a static potential to adjust the carrier concentration at the surface, (Garrett), or as a potential energy barrier to limit the charge transfer process.

DISCUSSION OF POSTULATES IN THE CHARGE TRANSFER THEORY

In the previous section, we have summarized the general approach to the rate process of charge transfer adsorption and/or desorption in terms of three postulates. We shall discuss the aforementioned postulates in this section.

I. On the Charge-Transfer Rate-Limiting Hypothesis

The first postulate in the charge transfer theory of adsorption and catalysis is that "charge transfer between the adsorbate and the solid adsorbent, a semiconductor, is the rate-limiting step". Now our first question: "Is this hypothesis plausible, or is it logically reasonable in the light of the recent observations on the semiconductor surface during adsorption? "

To answer this question, we shall consider the following adsorption of charged acceptors. Let A_n denote a molecule as it exists in gas phase. The adion is A^-. In the process of adsorption as A^-, we can visualize the following steps represented symbolically:

$$A_n(\text{gas}) \xrightarrow[(1)]{} A_n(\text{ads}) \xrightarrow[(2)]{} nA(\text{ads}) \xrightarrow[(3)]{} nA^- + ne^+ \tag{6.20}$$

The last step represents the charge transfer step, which involves the adatom A and an electron from the semiconductor adsorbent. Now a priori any one of the three steps, namely, (1) the molecular adsorption step, (2) the dissociation step, or (3) the ionization or charge transfer step, can be rate-limiting. Now if step (1) or (2) is slow or the rate-limiting step, it will be difficult to understand why the rate laws of adsorption are dependent on the typeness of semiconductor, since there is no interaction with the semiconductors which involves the carrier concentration. However, if step (3) is the rate-limiting step, the dependence of the rate laws of gas adsorption on the type of semiconductor can be easily understood, since the carrier concentration of the semiconductor is directly involved. Therefore, the charge transfer rate-limiting hypothesis is qualitatively, or intuitively plausible.

II. On the Activated Charge Transfer between the Semiconductor and the Adsorbate

In the previous development of the charge transfer theory of adsorption and catalysis, the charge transfer mechanism was always assumed to be activated, like thermionic emission. The wave mechanical tunneling process was not postulated. However, in semiconductor surface research the charge transfer between the semiconductor and slow surface states has also been postulated by the tunneling process by Kingston and others.(25). Lax(25) has pointed out the experimental contradictions to such a postulate. The main argument for a tunneling transfer process is that the slow changes in surface potential are independent of temperature. In addition to the data cited by Lax,(25) Morrison(26) and, more clearly, Liashenko and Litovchenko(27) have reported the temperature dependence of the slow relaxation process.

In view of the above cited observations, the postulate of activated or thermionic charge transfer is very plausible if not firmly established.

III. On the Evaluation and Application of Surface Potential by Poisson's Equation in One-Dimensional Form

The problem of using the solution of Poisson's equation in one-dimensional form has been discussed in Chapter 5. Here the physical situation is a different one. The difference arises from the fact that in dealing with the "adsorption isotherm" the total charge in the space charge region is time invariant. The space average diffusion potential, $Y(x)$,(28a) over the y-z plane at x, is equal to the time average in the case of adsorption-desorption equilibrium. This can be seen by considering the space average of the charged particle density ρ, since at any point in the space charge region, the continuity equation is presumed to hold

$$\nabla \cdot j_{\ell}(x, y, z) = -q \frac{\delta \rho(x, y, z)}{\delta t} \qquad (6.21)$$

where the subscript "ℓ " denotes a "local" point in the field, the space charge region. If we average $j_{\ell}(x, y, z)$ over the y-z plane at x, Equation (6.21) becomes

$$\frac{\delta j(x)}{\delta x} = -q \frac{\delta \rho(x)}{\delta t} \qquad (6.22)$$

Now at adsorption-desorption equilibrium, the net charge transfer between the semiconductor and the adsorbate is zero. That is, $j(0) = 0$, similarly $j(x) = 0$, and it follows that $\delta \rho(x)/\delta t = 0$. Therefore, $\rho(x)$, the space average charged particle density at x is independent of time and the problem is a static one as discussed in Chapter 5.

However, in treating the adsorption and/or desorption kinetics, the net rate of charge transfer between the semiconductor and the gas adsorbate is not zero. The left hand side of Equation (6.22) is not zero. This can be easily zeen by considering $j(\infty) = 0$, but $j(0) \neq 0$; i.e. the net rate of charge transfer at the surface is not zero. Therefore $j(x)$ varies from the surface to the bulk, and $\delta j(x)/\delta x \neq 0$. Consequently $\rho(x)$ is a function of time, and we shall write $\rho(x, t)$ from now on to denote the time dependent space average charged particle density, to distinguish it from the static case discussed in Chapter 5.

Now the question: "If the space average charge density, $q\rho(x, t)$, at any plane x is time dependent, is the surface potential, $Y(0)$, obtained by solving the static Poisson's equation applicable or sufficient to describe the rate of charge transfer? "

The answer to the above question depends on the velocity of electrons or holes transferred to or from the adsorbate, (or in other words, the rate of charge transfer). If the velocity of the charged particle is non-relativistic, (28b) it is sufficient to consider only the electric field, defined by a scalar potential function, which satisfies Poisson's equation.

In general the field equation in place of Poisson's equation is

$$\nabla^2 V_\ell - \frac{1}{c_m^2}\,\frac{\delta^2 V_\ell}{\delta t^2} = 4\pi\, q\, \rho_\ell\,(x, y, z, t)/\epsilon \tag{6.23}$$

where $c_m = c/\sqrt{\epsilon\mu}$, the velocity of the electromagnetic wave (i.e., light); μ is the magnetic permeability of the medium (i.e., the semiconductor), c is the ratio of e.m.u. to e.s.u. of charge, 2.998×10^{10}.

To appreciate why the rate of charge transfer has anything to do with the velocity of light in a semiconductor, we shall consider the extreme; that is $c_m \rightarrow \infty$. Then Equation (6.23) reduces to Poisson's equation of an electrostatic field. One can also reach such a conclusion by a consideration of the integrated result of Equation (6.23), which is given in standard text books,(29)

$$V_\ell\,(x', y', z', t) = \frac{1}{\epsilon}\iiint \frac{\rho_\ell[x, y, z, (t - r/c_m)]}{r}\,dx\,dy\,dz \tag{6.24}$$

where (x', y', z') is the field point, (x, y, z) is the source point; "r" = $[(x - x')^2 + (y - y')^2 + (z - z')^2]^{1/2}$. The integration is to be carried out with respect to (x, y, z).

The right hand of Equation (6.24) is called the retarded potential. That is, the contributions which the source makes to the potentials at a point (x', y', z') in the field do not arrive till after a time, r/c_m . When $c_m \rightarrow \infty$, Equation (6.24) reduces to the solution of a static field. Now what has this extreme case to do with our problem? To appreciate this, let us consider a cubic element with edge length, $r_c = 10^{-4}$ cm, cut from the <u>space charge region</u>, with one face of the cube corresponding to the original semiconductor surface. Then the longest linear dimension in the cube is $\sqrt{3}\,v_c = 1.7 \times 10^{-4}$ cm. The face of the cube which is the surface of the semiconductor has an area, $r_c^2 \simeq 10^{-8}$ cm^2. Assume that the area of one unit of the surface square lattice is $(3.33 \times 10^{-8}$ cm$)^2 \cong 10^{-15}$ cm^2. Then the original surface face of this small cube has 10^7 lattice sites. By assuming a monolayer coverage, the maximum ion density is that in which all the acceptors on the surface are charged, as A^-, and, it takes therefore 10^7 electrons. Since the saturation time is the order of minutes to hours,(26, 33) let us assume that it takes only one minute to fill the monolayer with 10^7 electrons. That is, the rate of electron transfer is $\sim 1.7 \times 10^5$ electrons/sec., or on the average one electron is transferred from the interior of the "cube" to its face in every 6×10^{-6} sec. The maximum electron velocity across the space charge region is about

$$v_e = 10^{-4} \text{ cm}/6 \times 10^{-6} = 17 \text{ cm/sec.}$$

Now assume that $\mu = 1$, $\epsilon = 16$, the magnetic wave velocity is, then, $c_m = (c/4)$ cm/sec. = 7.5×10^9 cm/sec. Since the longest linear dimension of the cube is 1.7×10^{-4} cm, the magnetic wave created when one electron is transferred from the space charge region to the surface will reach every point in the cube in a time interval, Δt, less than 2.3×10^{-14} sec. The time interval, 2.3×10^{-14} sec., is the "time lag" or "retarding time". If the magnetic wave velocity, c_m, is infinite the "retarding time" would be zero. However, since a second electron will not be transferred until 6×10^{-6} sec. later, which is 2.6×10^8 times greater than the "time lag" of 2.3×10^{-14} sec, the transfer of the second electron is <u>definitely</u> affected by the electrostatic potential, i.e., the diffusion potential, due to the previous electron transfer. The "time lag" is inconsequential as far as the transfer of the second electron is concerned. For the transfer of the second electron, the diffusion potential can be obtained by the solution of the Poisson's equation using the charge density before the second electron is transferred. Now let us inquire further into a question: "Does the electron experience a field due to the hole it left behind when the electron reaches the plane $x = 0$?"

To investigate this, we shall choose the field point (x', y', z') to be a point on the face of the "cube", which was cut from the space charge region. The face of the cube is on the plane $x = 0$. Therefore the field point is $(0', y', z')$, with y', z' on the face of the "cube". Now let us imagine that one electron-hole pair was located at a distance x from the surface, the electron is now moving toward the surface leaving the hole behind. Since on the average the time interval for the electron to travel from x to the surface bound by the face of the cube is 6×10^{-6} sec., (= $< x/v_e >$) , the magnetic wave will reach the field point at a time interval less than $(r_c^2 + x^2)^{1/2}/c_m \leqslant 2.3 \times 10^{-14}$ sec. Therefore the electron will also experience a field due to the hole it left behind as it crosses the plane $x = 0$. Therefore we can take c_m as infinitely large so that the electric field is instantaneously adjusted as far as the charge transfer to the surface is concerned. Consequently the second term on the left hand side of Equation (6.23) can be neglected. The resulting $\nabla^2 V_\ell$, when the space average over the y-z plane at x is taken becomes d^2V/dx^2. The result is Equation (6.26).

Another numerical estimation based on a different concept(30) will lead to the same result. For this analysis, Equation (6.23) is averaged over the y - x plane at x and t to obtain V(x, t),

$$\frac{\delta^2}{\delta x^2} V(x,t) - \frac{1}{c_m^2} \frac{\delta^2}{\delta t^2} V(x,t) = -(4\pi q/\epsilon)\, \rho(x,t) \qquad (6.25)$$

By numerical analysis(31) Equation (6.25) can be written as

$$\frac{V(x' + \Delta x, t') - 2V(x', t') + V(x' - \Delta x, t')}{(\Delta x)^2} \qquad (6.25a)$$

$$- \frac{V(x', t' + \Delta t) - 2V(x', t') + V(x', t' - \Delta t)}{c_m^2 (\Delta t)^2} = -(4\pi q/\epsilon)\, \rho(x', t')$$

Now we shall choose $x' = -L_s/2$ and $t' = \Delta t_s/2$, $\Delta x = L_s/2$ and $\Delta t = \Delta t_s/2$ where L_s and Δt_s are the depth of the space charge region and saturation time, respectively. Then since $V(-L_s, \Delta t_s) = 0$ and $V(L_s/2, 0) = 0$, Equation (6.25a) becomes

$$\frac{V(0, \Delta t_s/2) - 2V(-L_s/2, \Delta t_s/2)}{(L_s/2)^2} - \frac{V(-L_s/2, \Delta t_s) - 2V(-L_s/2, \Delta t_s/2)}{c_m^2 (\Delta t_s/2)^2}$$

$$= -(4\pi q/\epsilon)\, \rho(L_s/2, \Delta t/2) \qquad (6.25b)$$

Now since, $V(0, \Delta t_s/2) \lesssim V(0, \Delta t_s)$ and $V(-L/2, \Delta t_s) \lesssim V(0, \Delta t_s)$ the numerators of the two terms on the left hand side of Equation (6.25b) are about equal in magnitude; the relative magnitude of the two terms on the left hand side of Equation (6.25b) is determined by the magnitude of the denominators of the two terms. If the second term is to be negligible, we must have

$$(L_s/2)^2 << c_m^2 (\Delta t_s/2)^2$$

That is,

$$L_s << c_m \Delta t_s \tag{6.25c}$$

Now since, $L_s = 10^{-4}$ cm, $c_m = 7.5 \times 10^9$ cm/sec, and $\Delta t_c = 60$ sec., we have, $10^{-4} << 4.5 \times 10^{11}$. Therefore, the second term in Equation (6.25b) can be neglected. Since Equation (6.25b) is the difference representation of Equation (6.25), it follows that Equation (6.25) can be approximated by

$$\frac{d^2}{dx^2} V(x, t) = - (4\pi q/\epsilon) \rho(x, t) \tag{6.26}$$

Consequently it is concluded that the answer to the question posed at the beginning of this discussion is affirmative. The solution of Equation (6.26) is sufficient for this rate process. Therefore the previous treatments of the charge transfer problem by Garrett,(20) Weisz(4) and others are sufficient for the problem under consideration.

STATEMENT OF MODEL FOR ADSORPTION AND DESORPTION OF CHARGED PARTICLES

In the last section, we have discussed the plausibility of the basic assumptions in the kinetic theory of adsorption and desorption of gases on semiconductors. The assumption of a charge transfer rate-limiting process implies that the rate process concerned in this theory is the adsorption and desorption of charged particles. The model can best be represented in the following generalized symbolic equations.

I. Adsorption of Charged Particle Before Dissociation

For acceptors:

$$A_n(\text{gas}) \rightleftharpoons A_n(\text{ads}) \longrightarrow A_n^-(\text{Ads}) + e^+ \rightleftharpoons A^- + (n-1)A \tag{6.27a}$$

For donors:

$$D_n(\text{gas}) \rightleftharpoons D_n(\text{ads}) \longrightarrow D_n^+(\text{ads}) + e^- \rightleftharpoons D^+ + (n-1)D \tag{6.27b}$$

II. Adsorption of Charged Particle With Dissociation

For acceptors:

$$A_n(\text{gas}) \rightleftharpoons A_n(\text{ads}) \rightleftharpoons nA(\text{Ads}) \longrightarrow nA^-_{(\text{ads})} + ne^+ \tag{6.28a}$$

For donors:

$$D_n(\text{gas}) \rightleftharpoons D_n(\text{ads}) \rightleftharpoons nD(\text{ads}) \longrightarrow nD^+(\text{ads}) + ne^- \tag{6.28b}$$

III. Desorption of Molecular Ions

For acceptors:

$$A_n(\text{gas}) \rightleftharpoons A_n(\text{ads}) \longleftarrow A_n^-(\text{ads}) + e^+ \tag{6.29a}$$

For donors:

$$D_n(\text{gas}) \rightleftharpoons D_n(\text{ads}) \longleftarrow D_n^+(\text{ads}) + e^- \tag{6.29b}$$

IV. Desorption of Atomic Ions

For acceptors:

$$A_n(\text{gas}) \rightleftharpoons A_n(\text{ads}) \rightleftharpoons nA(\text{ads}) \longleftarrow nA^-(\text{ads}) + ne^+ \tag{6.30a}$$

For donors:

$$D_n(\text{gas}) \rightleftharpoons D_n(\text{ads}) \rightleftharpoons nD(\text{ads}) \longleftarrow nD^+(\text{ads}) + ne^- \tag{6.30b}$$

where the symbol "$\rightleftharpoons$" represent fast steps, and the symbol "$\longrightarrow$" represents the slow step or rate-limiting step. The implied assumption in the "charge transfer rate determining" postulate is that the species at either end of the symbol "$\rightleftharpoons$" are in equilibrium or "quasi-" equilibrium with one another and with the gas phase. The charged particles at the right end of the generalized symbolic equations are not in equilibrium with the gas phase. They increase with time toward the equilibrium surface concentration in an adsorption process or decrease with time toward "another equilibrium" in a desorption process.

From this understanding, it is clear that the rate theory requires that the physical situation be represented or approximately represented by the above generalized symbolic equations. The theoretical model requires the "presence" of the various uncharged particles adsorbed on the semiconductor surface, and further requires that the uncharged particles are in equilibrium or quasi-equilibrium with the gas phase. That is, the adsorption process of charged particles is preceeded by a fast process of adsorption of uncharged particles, which of course does not involve the carrier concentration of the semiconductor adsorbent. This picture is quite in accord with observations. Many authors(13, 33, 34) reported observations of initial fast adsorption, which precedes a slow adsorption. When gas up-take and electrical conductivity of the sample are measured at the same time, the "massive" initial gas up-take does not change the surface conductance.(33, 34)

The above statement combined with other postulates discussed in the previous section will be used in the remainder of this chapter for the formulation of the rate laws of adsorption and desorption of charged particles on semiconductors.

ON THE RATE OF CHARGE TRANSFER IN ADSORPTION AND DESORPTION OF CHARGED PARTICLES ON SEMICONDUCTORS

In the section on Literature Survey, we have discussed various models conceived by different authors. The rate functions for charge transfer across the surface "are most neatly and most generally written down by making use of the Hall-Shockley-Read model for trapping in a semiconductor", as stated and carried out by Garrett.(20) Garrett's Equations (4) and (5) can be written in the following form.

The rate of electron transfer from the semiconductor is the sum of electron transfer from both the conduction band and the valence band

$$R(\uparrow) = R_c(\uparrow) + R_v(\uparrow) \qquad (6.31)$$

where $R_c(\uparrow) = [A]\, c_{n,A}\, n_s - [A^-]\, c_{n,A}\, n_{1,A}$ (6.32)

$$R_v(\uparrow) = [A]\, c_{p,A}\, p_{1.A} - [A^-]\, c_{p,A}\, p_s \qquad (6.33)$$

Similarly the rate of electron transfer into the semiconductor can be written as

$$R(\downarrow) = R_c(\downarrow) + R_v(\downarrow) \qquad (6.34)$$

where

$$R_c(\downarrow) = [A^-]\, c_{n,D}\, n_{1,D} - [A]\, c_{n,D}\, n_s \qquad (6.35)$$

$$R_v(\downarrow) = [A^-]\, c_{p,D}\, p_s - [A]\, c_{p,D}\, p_{1,D} \qquad (6.36)$$

Equation (6.31) is equivalent to Equation (5) in Garrett's paper, which expresses the rate of electron transfer from the semiconductor to the acceptor, A. The terms $R_c(\uparrow)$ and $R_v(\uparrow)$ express respectively the rate of electron transfer from the conduction band and valence band to the acceptor. Equations (6.32) and (6.33) are written in a form which is equivalent to Equations (3.8) and (3.9) in the Shockley-Read(22) paper. It is fairly obvious that Equation (6.31) corresponds to the rate of adsorption of charged particles, A^-. Equation (6.34) is equivalent to Equation

(4) in Garrett's paper. The terms $R_c(\downarrow)$ and $R_v(\downarrow)$ express the rate of electron transfer to the conduction and valence band, respectively. The factors $c_{n,A}, c_{p,A}$ are constants; n_s, p_s are the electron and hole concentration at the surface; and $n_{1,A}, p_{1,A}$ are defined by the following equations:

$$n_{1,A} = N_c \exp(E_A - E_c)/kT \qquad (6.37a)$$

$$p_{1,A} = N_v \exp(E_v - E_A)/kT \qquad (6.37b)$$

That is, $n_{1,A}$ and $p_{1,A}$ are the respective electron and hole concentrations when the Fermi level coincides with the acceptor level, E_A.

The rate equation for charge transfer to and from donors can be simply obtained by replacing $[A^-]$ with $[D]$, $[A]$ with $[D^+]$, and the acceptor level by the donor level, E_D. Due to the similarity, we shall treat the case of adsorption and desorption of acceptors only, the case of adsorption and desorption donors should follow by analogy with that of acceptors.

Now before we apply Equations (6.31) to (6.36) in treating the kinetics of adsorption and desorption of charged particles, one more inquiry has to be made. Namely, is the Shockley-Read model valid in this case, since it was originally derived to express the rate of electron and hole recombination via traps in the bulk. That is, the charge transfer to and from the "trapping centers" was assumed to be in a three-dimensional space. In applying this theory to charge transfer between the semiconductor and the surface ad-particles, the charge transfer is only in one direction. That is, only electrons which move in the x-direction and cross the plane, $x = 0$ (the surface plane), can be trapped or emitted. Now the question: "Does this unidirectional charge transfer affect the rate equations for charge transfer as written down by Garrett, and reproduced as Equations (6.32), (6.33), (6.35) and (6.36)?"

We shall show that the rate equations are not changed, i.e., Garrett's rate equations are correct. To see this, we have to go back to the original Shockley-Read model.(23) Now let us follow the procedure of the Shockley-Read paper, defining $F(E)$ as the probability that a quantum state of energy level E is occupied, and $F_p(E)$ as the probability that the state is empty. Therefore,

$F(E) = 1/\left\{1 + \exp(E^* - E_f)/kT\right\}$

$F_p(E) = 1 - F(E) = F(E) \exp(E^* - E_f)/kT.$

$E^* = E - Y_s$, the modified energy level in the space charge region.

$v_x(E)$ = electron velocity in x-direction with energy, E.

$\sigma_c(E)$ = capture cross section for electron with energy, E.

$\sigma_e(E)$ = emission cross section for electron with energy, E.

$S(E)dE$ = number of quantum states per cm^3 in $(E, E + dE)$.

$[A]$ = number of unfilled traps per cm^2.

$[A^-]$ = number of filled traps per cm^2.

Then, the gross rate of electron capture is,

gross electron capture rate = $[A]\, \sigma_c v_x S(E) F(E) dE$

Rate of emission is,

gross electron emission rate = $[A^-]\, \sigma_e v_x S(E) F_p(E) dE$

The net rate of electron capture from the conduction band is:

$$dR_c(\uparrow) = \left\{[A] - [A^-]\frac{e_n}{c_n}\frac{F_p(E)}{F(E)}\right\} \sigma_c v_x (E) F(E) dE \qquad (6.38)$$

where c_n = average of $<v_x><\sigma_c>$ for all E.

e_n = emission constant corresponding to c_n (see Shockley and Read).

Equation (6.38) corresponds to Equation (2.8) of the Shockley-Read paper. Using the quasi-Fermi level concept as proposed by Shockley and Read, E_f is written as $E_f^{(n)}$ for the semiconductor and $E_f^{(t)}$ for the acceptor. At thermodynamic equilibrium,

$$E_f^{(n)} = E_f^{(t)} = E_f \qquad (6.38a)$$

Furthermore, if we assume that the electron spin on $[A^-]$ is uncompensated, the distribution function becomes

$$\frac{[A^-]}{[A] + [A^-]} = \frac{1}{1 + (1/2)\exp[(E_A^* - E_f^{(t)})/kT]} \qquad (6.38b)$$

where $E_A^* = E_A + Y_s$

or

$$[A]/[A^-] = (1/2)\exp[(E_A^* - E_f^{(t)})/kT] \qquad (6.38c)$$

When the electron transfer rate between E_A^* and E^* is zero, then it follows from Equation (6.38) and the preceding definitions that

$$(e_n/c_n) = \frac{[A]}{[A^-]}\frac{F(E)}{F_p(E)} = (1/2)\exp\left\{(E_A^* - E^*)/kT\right\}$$

$$= (1/2)\exp\left\{(E_A - E/kT\right\} \qquad (6.38d)$$

Equation (6.38d) is Shockley-Read's Equation (2.9). Now substitute Equation (6.38d) into Equation (6.38). At any condition we have

$$dR_c(\uparrow) = \left\{[A] - (1/2)[A^-]\exp[(E_A^* - E_f^{(n)})/kT]\right\}\sigma_c v_x S(E)F(E)dE$$

$$(6.38e)$$

Equation (6.38e) is equivalent to Shockley-Read's Equation (2.10), which can be easily obtained by combining with Equation (6.38b).

For a non-degenerate semiconductor Equation (6.38e) can be integrated following a procedure similar to that which was used in Equations (4.13) to (4.18) of Chapter 4. For $E_A < E_c$, the integration is from $v_x = 0$ to $v_x = \infty$. Then the result is

$$R_c(\uparrow) = \left\{ [A] - (1/2)[A^-] \exp[(E_A^* - E_f^{(n)})/kT] \right\}$$

$$\cdot <\sigma_c> \frac{4\pi m^* k^2 T^2}{h^3} \exp - \left\{ [E_c^* - E_f^{(n)}]/kT \right\} \qquad (6.38f)$$

where $<\sigma_c>$ is average capture cross section for electrons from conduction band.

Equation (6.38f) can be written as,

$$R_c(\uparrow) = \left\{ [A] - (1/2)[A^-] \exp[(E_A^* - E_f^{(n)})/kT] \right\}$$

$$\cdot <\sigma_c> (kT/2\pi m^*)^{1/2} N_c \exp \left\{ - [E_c^* - E_f^{(n)}]/kT \right\} \qquad (6.38g)$$

Now $(kT/2\pi m^*)^{1/2} = <v_x>$, the average electron velocity in x-direction. If we write $c_{n,A} = <\sigma_c> \cdot <v_x>$, Equation (6.38g) can be written as

$$R_c(\uparrow) = [A]\, c_{n,A} n_s = (1/2)[A^-]\, c_{n,A} N_c \exp \left\{ (E_A^* - E_c^*)/kT \right\} \qquad (6.39)$$

Since $E_A^* - E_c^* = E_A - E_c$, Equation (6.39) reduces to

$$R_c(\uparrow) = [A]\, c_{n,A} n_s - (1/2)[A^-]\, c_{n,A} n_{1,A} \qquad (6.39a)$$

Equation (6.39a) is the same as Equation (6.32) except for the factor 1/2, which takes account of the uncompensated spin on $[A^-]$. Therefore the Equations (6.32), (6.33), (6.35) and (6.36) should have the following form

$$R_c(\uparrow) = [A]\, c_{n,A} n_s - (1/2)[A^-]\, c_{n,A} n_{1,A} \qquad (6.32a)$$

$$R_v(\uparrow) = [A]\, c_{p,A} p_{1,A} - (1/2)[A^-]\, c_{p,A} p_s \qquad (6.33a)$$

$$R_c(\downarrow) = (1/2)[A^-]\, c_{n,D}\, n_{1,D} - [A]\, c_{n,D}\, n_s \qquad (6.35a)$$

$$R_v(\downarrow) = (1/2)[A^-]\, c_{p,D}\, p_s - [A]\, c_{p,D}\, p_{1,D} \qquad (6.36a)$$

For the remainder of this chapter Equations (6.32a), (6.33a), (6.35a) and (6.36a) will be used to derive the rate equations of adsorption and desorption of charged particles. Furthermore, for the adsorption or desorption of molecular ions, $[A^-]$ should be replaced by $[A_n^-]$, and $[A]$ by $[A_n]$, etc. The final resulting rate equations can also be obtained by the above replacement.

FORMULATION OF RATE EQUATIONS FOR ADSORPTION OF CHARGED PARTICLES

In this section, the rate equations for adsorption of charged particles will be derived. For convenience of presentation, space charge regions are used to classify the subsections. The fundamental equations for adsorption are:

$$\frac{d}{dt}[A^-] = R_c(\uparrow) + R_v(\uparrow) \qquad (6.40a)$$

$$\frac{d}{dt}[D^+] = R_c(\downarrow) + R_v(\downarrow) \qquad (6.40b)$$

where $R_c(\uparrow)$ and $R_v(\uparrow)$ are given by (6.32a) and (6.33a); $R_c(\downarrow)$, $R_v(\downarrow)$ are given by Equations (6.35a) and (6.36a) with $[A^-]$ replaced by $[D]$, and $[A]$ replaced by $[D^+]$.

To save space, we shall treat the adsorption of acceptors only. The counterpart, adsorption of donors, will be given without analysis.

Rate Laws Associated With Accumulation Space Charge Regions

This subsection is further divided into adsorption on an intrinsic semiconductor and adsorption on an extrinsic semiconductor.

Adsorption on an Intrinsic Semiconductor

We shall use Equation (6.40) together with the following equations from Chapter 2:

$$u_s = Y_s/kT = (L_m/n_i)^{1/2}[D^+] \leqslant 0.9 \tag{2.20}$$

$$u_s' = Y_s'/kT = (L_m/n_i)^{1/2}[A^-] \leqslant 0.9 \tag{2.20'}$$

$$u_s = Y_s/kT = \ln\left\{(L_m/n_i)[D^+]^2\right\} \tag{2.21}$$

$$u_s' = Y_s'/kT = \ln\left\{(L_m/n_i)[A^-]^2\right\} \tag{2.21'}$$

For the convenience of presentation we shall divide this section into two cases. The first case corresponds to u_s' represented by Equation (2.20') and is defined as the initial stage of adsorption. The second case corresponds to Equation (2.21') and is the high coverage stage.

In the initial stage, the reverse process, (i.e., desorption), is negligible. Equation (6.40a) can be written as

$$\frac{d}{dt}[A^-] = c_{n,A}[A]\, n_s + c_{p,A}\, p_{1,A}\, [A] \tag{6.41a}$$

Now let us consider the rate process a little more. As adsorption starts, the surface charge $[A^-]$ increases. Equation (6.26) says that $u_s'(t)$ can be evaluated by $[A^-](t)$, therefore $n_s(t)$ is a function of $[A^-](t)$. Then Equation (6.41a) can be written in terms of $[A^-]$ from Equation (2.20'), which is a function of time.

$$\frac{d[A^-]}{dt} = c_{n,A}\, n_i [A] \exp\left\{-(L_m/n_i)^{1/2}[A^-]\right\} + [A]\, c_{p,A}\, p_{1,A} \tag{6.41a'}$$

where n_i is the bulk hole or electron concentration. From our discussions in the "Model" section, $[A]$ is a function of the gas pressure only. Therefore in an isobaric process $[A]$ is independent of time. In an isosteric process $[A]$ is a function of time because the gas phase pressure decreases with time, and Equation (6.41a') can not be integrated. It is rather unfortunate, because a large amount of reported data in the literature were taken in an isosteric condition. Equation (6.41a) is miserable enough without experimentally introduced variations!

Now let us consider an isobaric process. The relative magnitude of the two terms on the right hand side of Equation (6.41a') determines the form of rate law of adsorption. For example: if the first term is small, the rate law is linear, i.e., $[A^-] \propto t$. If the second term is small, the rate law is logarithmic. The question becomes, "What determines the relative magnitude of the two terms on the right hand side of Equation (6.41a')?" Of course, it is determined by the factors in the respective terms!

Since $c_{n,A}$ and $c_{p,A}$ are the products of the average capture cross section and the velocity, $c_{n,A}$ is always larger than $c_{p,A}$. For n_i and $p_{1,A}$, n_i is determined by the bulk energy gap, E_g; $p_{1,A}$ is determined by $(E_A - E_V)$, [see Equation (6.37b)] . That is, if E_A is close to E_f, n_i will be close to $p_{1,A}$. Therefore, when E_A is close to the middle of the energy gap, the first term on the right hand side of Equation (6.41a) is always larger than the second term, since $c_{n,A}$ is in general much larger than $c_{p,A}$. Under this condition Equation (6.41a) can be approximated by

$$\frac{d}{dt}[A^-] \cong [A]\, c_{n,A}\, n_i \exp\left\{-(L_m/n_i)^{1/2}[A^-]\right\} \qquad (6.42a)$$

Equation (6.42a) can be integrated under isobaric conditions in which $[A] = K_a (P_{A_n})^{1/n}$ is independent of time.

$$[A^-] = (n_i/L_m)^{1/2} \ln\left\{1 + [A]\, c_{n,A} (n_i L_m)^{1/2} t\right\} \qquad (6.41a')$$

For adsorption of donors on intrinsic semiconductors the corresponding results are:

$$\frac{d}{dt}[D^+] = (c_{n,D}\, n_{1,D}/2)\,[D] + (c_{p,D}\, n_i/2)\,[D]\, \exp\left\{-(L_m/n_i)^{1/2}\,[D^+]\right\} \qquad (6.41b)$$

When $R_V(\uparrow) \gg R_C(\uparrow)$, (the donor level is very deep), the integration of the exponential term gives

$$[D^+] \cong (n_i/L_m)^{1/2} \ln\left\{1 + [D]\, c_{p,D}(L_m n_i)^{1/2}\, t/2\right\} \qquad (6.41b')$$

In the <u>high coverage stage</u> $u_s' = \ln\left\{(L_m/n_i)\,[A^-]^2\right\} \geqslant 2$, and the general expression is obtained by making use of Equations (6.32a) and (6.33a).

$$\frac{d[A^-]}{dt} = [A]\left\{c_{n,A}\, n_i \exp(-u_s') + c_{p,A}\, p_{1,A}\right\} - \frac{1}{2}[A^-]\left\{c_{n,A}\, n_{1,A} + c_{p,A}\, n_i \exp(u_s')\right\} \qquad (6.43a)$$

In the case that $R_V(\uparrow) \gg R_C(\uparrow)$, i.e., the surface region is highly p-type, Equation (6.43a) can be approximated by

$$\frac{d}{dt}[A^-] = c_{p,A}\, p_{1,A}\,[A] - (c_{p,A}\, L_m/2)\,[A^-]^3 \qquad (6.44a)$$

Under isobaric conditions, where $[A]$ is independent of time, Equation (6.44a) can be integrated into the following series

$$\sum_{n=0}^{\infty} \frac{1}{3n+1}\,(L_m/2\,p_{1,A}\,[A])^n\,[A^-]^{3n+1}$$

$$\cong [A]\, c_{p,A}\, p_{1,A}\, t + \text{const.} \qquad (6.45a)$$

The integration constant arises from the fact that Equation (6.45a) is an approximation for $u_s' \geqslant 2$.

For donors on intrinsic semiconductors, the counterpart equations can be obtained from Equations (6.35a) and (6.36a). These are

$$\frac{d[D^+]}{dt} = \frac{1}{2}[D]\left\{c_{p,D}\,p_i \exp(-u_s) + c_{n,D}\,n_{1,D}\right\}$$

$$- [D^+]\left\{c_{p,D}\,p_{1,D} + c_{n,D}\,n_i \exp(u_s)\right\} \qquad (6.43b)$$

Under the condition that $R_c(\downarrow) >> R_v(\downarrow)$ an equation similar to Equation (6.45a) can be obtained.

$$\sum_{n=0}^{\infty} \frac{1}{3n+1}\left(\frac{2L_m}{[D]\,n_{1,D}}\right)^n [D^+]^{3n+1}$$

$$= ([D]\,c_{n,D}\,n_{1,D}/2)t + \text{const.} \qquad (6.45b)$$

Adsorption on an Extrinsic Semiconductor

For the adsorption of acceptors on p-type semiconductors, the electrons "trapped" by the surface acceptors are mainly from the valence band. We can safely assume that $R_v(\uparrow) >> R_c(\uparrow)$ at high surface coverage.

For the derivation of the rate laws, we shall make use of Equation (6.40a) together with the following equations:

$$u_s' = (L_m/p_B)^{1/2}[A^-] \leqslant 0.9 \qquad (2.34a)$$

$$u_s' = \ln\left\{(L_m/p_B)[A^-]^2\right\} \geqslant 2 \qquad (2.37a)$$

Therefore Equation (6.40a) can be written as

$$\frac{d}{dt}[A^-] \cong [A]\,c_{p,A}\,p_{1,A} - (1/2)[A^-]\,c_{p,A}\,p_s \qquad (6.40a')$$

At the initial stage of adsorption the second term on the right hand side of Equation (6.40a') can be neglected. The rate is, therefore, linear. For high coverage, Equation (6.40a') is combined with Equation (2.37a), and the derivation is similar to that of Equation (6.45a). The result is

$$\sum_{n=0}^{\infty} \frac{1}{3n+1}\left(\frac{L_m}{2p_{1,A}[A]}\right)^{n} [A^-]^{3n+1} = [A]\, c_{p,A}\, p_{1,A}\, t \qquad (6.46a)$$

It should be noted that when $n = 0$, Equation (6.46a) reduces to the rate equations for low coverage or the initial stage of adsorption.

When donors on an n-type semiconductor are considered, the result is

$$\sum_{n=0}^{\infty} \frac{1}{3n+1}\left(\frac{2L_m}{[D]\, n_{1,D}}\right)^{n} [D^+]^{3n+1} = ([D]\, c_{n,D}\, n_{1,D}/2)\, t$$

(6.46b)

Rate Laws Associated with Depletion-Inversion Space Charge Regions

The adsorption of acceptors on n-type semiconductors (or donors on p-type semiconductors) will produce first a slight depletion-inversion space region, and finally a strong inversion region. The classification of these regions has been discussed in Chapter 2.

In the following analysis, we shall derive the rate laws for adsorption of acceptors on an n-type semiconductor in detail. Only the result for the adsorption of donors on a p-type semiconductor will be given. Together with Equation (6.40a), the following equations will be used:

$$u_s' = [2L_m/(n_B + p_B)]^{1/2}[A^-] \leq 0.9$$

$$u_s' = m'(L_m/n_B)^{1/2}[A^-] - b \qquad (5.71)$$

where u_s' in Equation (5.71) must be:

$$u_B - 1 \leqslant u_s' \leqslant (2u_B + 1)$$

where m' and b are given in Equations (5.27) and (5.27a) of Chapter 5.

For convenience of presentation, we shall divide this section into three subsections, namely: the slight depletion region, the depletion-inversion region, and the strong inversion region.

Slight Depletion Region

The slight depletion space charge region is defined by Equation (2.46). At this initial stage the electrons transferred to the acceptors are from the conduction band; therefore, $R_c(\uparrow) >> R_v(\uparrow)$. Then Equation (6.40a) can be written as,

$$\frac{d}{dt}[A^-] \cong c_{n,A} n_B [A] \exp(-u_s') - (c_{n,A} n_{1,A}/2)[A^-] \qquad (6.47a)$$

Since $[A^-]$ is very small, the reverse reaction can be neglected. When this is done, and Equation (6.47a) is combined with Equation (2.46), the following equation results.

$$\frac{d}{dt}[A^-] = c_{n,A} n_B [A] \exp\left\{-[2L_m/(n_B + p_B)]^{1/2}[A^-]\right\} \qquad (6.48a)^*$$

Under isobaric conditions, Equation (6.48a) can be integrated:

$$[A^-] = [(n_B + p_B)/2L_m]^{1/2} \ln\left\{1 + [A] c_{n,A} n_B [(L_m/(n_B + p_B)]^{1/2} t\right\} \qquad (6.48a')$$

For donors on p-type semiconductors the results are

$$\frac{d[D^+]}{dt} = (c_{p,D} p_B/2)[D] \exp\left\{-[2L_m/(n_B + p_B)][D^+]\right\} \qquad (6.48b)$$

---

* An equation similar to Equation (6.48a) has been obtained by Barry and Stone (see Literature Survey).

and

$$[D^+] = \left[\frac{(n_B + p_B)}{2L_m}\right]^{1/2} \ln\left\{1 + [D]\, c_{p,D}\, p_B \left[\frac{L_m}{2(n_B + p_B)}\right] t\right\} \qquad (6.48b')$$

Depletion-Inversion Region

For acceptors on n-type semiconductors, the general rate expression is:

$$\frac{d}{dt}[A^-] = [A]\left\{c_{n,A}\, n_s + c_{p,A}\, p_{1,A}\right\}$$

$$- [A^-]\left\{c_{n,A}\, n_{1,A} + c_{p,A}\, p_s\right\} / 2 \qquad (6.49a)$$

Under the condition that $R_c(\uparrow) > R_v(\uparrow)$ and that the reverse reaction can be neglected, Equation (6.49a) in combination with Equation (5.71) gives

$$\frac{d}{dt}[A^-] \cong (c'_{n,A}\, n_B)\,[A] \quad \exp\left\{- B_n\,[A^-]\right\} \qquad (6.50a)$$

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

and $c'_{n,A} = c_{n,A} \exp\,(b)$ (6.51a)

Under isobaric conditions, Equation (6.50a) can be integrated to give

$$[A^-] = (1/B_n) \ln\left\{1 + B_n\, c'_{n,A}\, n_B\, [A]\, t\right\} \qquad (6.52a)$$

When $B_n\, c'_{n,A}\, n_B [A]\, t >> 1$, Equation (6.52a) can be further simplified to the following equation.

$$[A^-] \cong (1/B_n) \ \ln t + Z_n \qquad (6.53a)$$

where $Z_n \equiv (1/B_n) \ \ln\left\{B_n\, [A]\, c'_{n,Z}\, n_B\right\}$ (6.54a)

In general, if $R_v(\uparrow)$ can not be neglected, Equation (6.49a) can be written as

$$\frac{d}{dt}[A^-] \cong c'_{n,A} n_B [A] \exp\left\{-B_n [A^-]\right\} + [A]\, c_{p,A} p_{1,A} \tag{6.55a}$$

The integrated result of Equation (6.55a) gives

$$\ln\left\{1 + \frac{c_{p,A} p_{1,A}}{c'_{n,A} n_B} \exp\left(B_n [A^-]\right)\right\}$$

$$= B_n [A] c_{p,A} p_{1,A} t - \ln\left\{c'_{n,A} n_B [A]\right\} \tag{6.56a}$$

Note that Equation (6.56a) reduces to an equation of the form of Equation (6.53a) when the second term in the logarithm on the left hand side is less than one.

For donors on p-type semiconductors the results are

$$\frac{d[D^+]}{dt} = (c'_{p,D} p_B/2)\,[D] \exp\left\{-B_p [D^+]\right\} \tag{6.50a}$$

where $c'_{p,D} = c_{p,D} \exp(b)$

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

Integration gives

$$[D^+] \cong (1/B_p) \ln\left\{1 + B_p c'_{p,D} p_B [D]\, t/2\right\} \tag{6.52b}$$

which can also be written as

$$[D^+] \cong (1/B_p) \ln t + Z_p \tag{6.51b}$$

where,
$$Z_p = (1/B_p) \ln\left\{B_p [D]\, c'_{p,D} p_B/2\right\} \tag{6.53b}$$

When $R_c(\downarrow)$ is not negligible:

$$\frac{d}{dt}[D^+] \cong (c'_{p,D} p_B [D]/2) \exp\left\{-B_p [D^+]\right\} + [D]\, c_{n,D} n_{1,D}/2$$

Integration gives

$$\ln\left\{1 + \frac{c_{n,D}\, n_{1,D}}{c'_{p,D}\, p_B} \exp\, (B_p [D^+]\right\}$$

$$= B_p\, [D]\, c_{n,D}\, n_{1,D}\, t/2 - \ln\left\{c'_{p,D}\, p_B [D]/2\right\} \qquad (6.56b)$$

Strong Inversion Space Charge Region

The rate equations for this situation are exactly like those of Equations (6.46a) and (6.46b). We shall omit the repetition.

FORMULATION OF RATE EQUATIONS FOR DESORPTION OF CHARGED PARTICLES

The desorption process is the reverse of the adsorption process, which has been treated in the last section. For the formulation of rate laws of desorption of charged particles, the starting equations are:

For desorption of A^-

$$-\frac{d}{dt}[A^-] = R_c(\downarrow) + R_v(\downarrow) \qquad (6.57a)$$

For desorption of D^+

$$-\frac{d}{dt}[D^+] = R_c(\uparrow) + R_v(\uparrow) \qquad (6.57b)$$

where $R_c(\downarrow)$ and $R_v(\downarrow)$ are given by Equations (6.35a) and (6.36a); $R_c(\uparrow)$ and $R_v(\uparrow)$ are given by Equations (6.32a) and (6.33a) with $[A]$ replaced by $[D^+]$, and $[A^-]$ replaced by $[D]$. Due to the similarity for the desorption of positive adions, $[D^+]$, and negative adions, $[A^-]$, we we shall treat the desorption of negative adions only. The rate laws for the desorption of $[D^+]$ will be given by analogy.

Rate Equations of Desorption of Adions

Associated with an Accumulation Space Charge Region

This section is further divided into desorption from an intrinsic semiconductor, and desorption from an extrinsic semiconductor.

Desorption of Adions from an Intrinsic Semiconductor

The desorption process should tend to restore the straight band condition by transferring the electrons back to the semiconductor. Now let us imagine an intrinsic semiconductor with A^- ions adsorbed on its surface. When the space surrounding the semiconductor surface is under a high vacuum or when the temperature of the system is changed, the uncharged ad-particles will be desorbed, first quickly to a new surface concentration in equilibrium with the pressure at the new condition, then more slowly toward the new equilibrium. Therefore, the initial stage of desorption of adions corresponds to the high surface coverage of adions; the final stage corresponds to the low surface coverage of adions.

For the formulation of the rate equations for desorption of adions, $[A^-]$, we shall make use of Equation (6.57a) and Equation (2.37a).

For simplifying the treatment, we shall assume that the new condition is such that the surface of the semiconductor corresponds to a "clean" surface, i.e., $[A] \cong 0$. Consequently, the reverse reaction in Equation (6.57a) can be neglected.

At the initial stage of desorption Equation (6.57a) can be written as

$$-\frac{d}{dt}[A^-] \cong (c_{p,D}L_m/2)[A^-]^3 + (c_{n,D}n_{1,D}/2)[A^-] \qquad (6.58a)$$

For the convenience of representation let,

$$d_p = c_{p,D}L_m/2 \qquad (6.59a)$$

$$d_n = c_{n,D}n_{1,D}/2 \qquad (6.60a)$$

Therefore, Equation (6.58a) can be written as,

$$-\frac{d}{dt}[A^-] \cong d_p[A^-]^3 + d_n[A^-] \tag{6.58a'}$$

The integrated form of the equation is:

$$\ln\left\{\frac{[A^-]_o(d_p[A^-]^2 + d_n)}{[A^-](d_p[A^-]_o^2 + d_n)}\right\} \cong 2d_n t \tag{6.61a}$$

where the limits of integration have been chosen as $[A^-] = [A^-]_o$ when $t = 0$.

It is possible that at the beginning of desorption $R_v(\downarrow) >> R_c(\downarrow)$, and then Equation (6.58a') can be simplified to,

$$-\frac{d}{dt}[A^-] \cong d_p[A^-]^3 \tag{6.62a}$$

By integrating Equation (6.62a), the following equation is obtained.

$$[A^-] \cong \frac{[A^-]_o}{\left\{1 + 2[A^-]_o d_p t\right\}^{1/2}} \tag{6.62a'}$$

It is interesting to note that Equation (6.62a') is the Becquerel hyperbola.

For donors desorbing from intrinsic semiconductors, the results are:

$$-\frac{d}{dt}[D^+] = (c_{n,A}L_m)[D^+]^3 + c_{p,A}p_{1,A}[D^+] \tag{6.58b}$$

The integrated form of the equation is

$$\ln\left\{\frac{[D^+]_o(d'_n[D^+]^2 + d'_p)}{[D^+](d'_n[D^+]_o^2 + d'_p)}\right\} = 2d'_p t \tag{6.61b}$$

where:

$$d'_n = c_{n,A} L_m \tag{6.59b}$$

$$d'_p = c_{p,A} p_{1,A} \tag{6.60b}$$

In the case that $R_c(\uparrow) >> R_v(\uparrow)$

$$-\frac{d}{dt}[D^+] \cong d'_n [D^+]^3 \tag{6.62b}$$

The integrated form is:

$$[D^+] \cong \frac{[D^+]_o}{\left\{1 + 2[D^+]_o d'_n t\right\}^{1/2}} \tag{6.62b'}$$

For the final stage of desorption, the starting point of this derivation is still Equation (6.57a). If the reverse rate is still negligible, we shall have

$$-\frac{d}{dt}[A^-] \cong (c_{p,D} n_i/2)[A^-] \exp\left\{(L_m/n_i)^{1/2}[A^-]\right\}$$

$$+ (c_{n,D} n_{1,D}/2)[A^-] \tag{6.63a}$$

This equation is not easily integrated analytically in simple form.

Desorption of Adions from an Extrinsic Semiconductor

During the initial stage for the desorption of negative adions from a p-type semiconductor the space charge region changes from strongly p-type to moderately p-type in this case, and $R_v(\downarrow) >> R_c(\downarrow)$. The rate of desorption can be derived by applying Equations (6.57a) and (2.37a). The differential rate equation is:

$$-\frac{d}{dt}[A^-] \cong (c_{p,D} L_m/2)[A^-]^3 = d_p [A^-]^3 \tag{6.64a}$$

Equation (6.64a) is the same as Equation (6.62a). The integrated result will be the same as Equation (6.62a').

For the desorption of positive adions from an n-type semiconductor, the result is given by Equations (6.62b) and (6.62b').

For the final stage of desorption of negative adions from p-type semiconductors, the surface ion concentration is such that $u'_s < 0.9$. The rate equation can be written by making use of Equations (6.57a) and (2.34a).

$$- \frac{d}{dt}[A^-] \cong [A^-]\,(c_{p,D}\,p_B/2)\,\exp\left\{(L_m/p_B)^{1/2}[A^-]\right\} \tag{6.65a}$$

Equation (6.65a) can be integrated by expansion of the exponential. The result is

$$\ln\frac{[A^-]}{[A^-]_o} + \sum_{n=1}^{\infty}\frac{1}{n!\cdot n}\left\{(L_m/p_B)^{n/2}([A^-] - [A^-]_o)\right\}$$

$$\cong (c_{p,D}\,p_B/2)\,(t - t_o) \tag{6.66a}$$

where $[A^-] = [A^-]_o$, when $t = t_o$, and $u'_s \leqslant 0.9$.

The first term approximation gives:

$$[A^-] \cong [A^-]_o\,\exp\left\{-(c_{p,D}\,p_B/2)\,(t - t_o)\right\} \tag{6.67a}$$

Note that Equation (6.67a) is the exponential decay formula.

For desorption of positive adions from n-type semiconductors, the results are

$$- \frac{d}{dt}[D^+] \cong [D^+]\,c_{n,A}\,n_B\,\exp\left\{(L_m/n_B)^{1/2}[D^+]\right\} \tag{6.65b}$$

Integration gives

$$\ln\frac{[D^+]}{[D^+]_o} + \sum_{n=1}^{\infty}\frac{1}{n!\cdot n}\left\{(L_m/n_B)^{n/2}([D^+] - [D^+]_o)\right\} = c_{n,A}\,n_B\,(t - t_o) \tag{6.66b}$$

and the first term only is

$$[D^+] \cong [D^+]_o \exp\left\{c_{n,A} n_B (t - t_o)\right\} \qquad (6.67b)$$

Rate Equations of Desorption Associated With a Depletion-Inversion Space Charge Region

For completeness, we shall assume that the desorption process starts from an adion concentration such that a strongly inverted space charge region is generated in the semiconductor.

Desorption from a Strong Inversion Space Charge Region

The rate equations for desorption of negative adions from n-type semiconductors are the same as Equations (6.64a) or (6.62a) and (6.62a').

The rate equations for desorption of positive adions from p-type semiconductors are the same as Equations (6.62b) and (6.62b').

Desorption from a Moderate Depletion-Inversion Space Charge Region

For the desorption of negative adions from n-type semiconductors Equation (6.57a) can be written as,

$$-\frac{d}{dt}[A^-] = (1/2)[A^-]\left\{c_{n,D} n_{1,D} + c_{p,D} p_s\right\} \qquad (6.68a)$$

For the depletion-inversion region, u'_s is given by Equation (5.71) where $2u_B + 1 \geqslant u'_s > u_B - 1$. Substituting u'_s into Equation (6.68a) gives

$$-\frac{d[A^-]}{dt} = ([A^-]/2)\left\{c_{n,D} n_{1,D} + c'_{p,D} p_B \exp(B_n[A^-])\right\} \qquad (6.69a)$$

where $c'_{p,D} = c_{p,D} \exp(-b)$

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

There are two extreme cases in Equation (6.69a), namely,

$$\text{(i)}\ R_V(\downarrow) >> R_C(\downarrow) \quad \text{and (ii)}\ R_C(\downarrow) >> R_V(\downarrow)\ .$$

For case (i),

$$-\frac{d[A^-]}{dt} \cong (c'_{p,D}p_B/2)\,[A^-]\ \exp\left\{B_n[A^-]\right\} \qquad (6.70a)$$

Let $[A^-] = [A^-]_o$ at $t = 0$. Equation (6.70a) can be written,

$$-\frac{d}{dt}\frac{[A^-]}{[A^-]_o} \cong (c'_{p,D}p_B/2)\,\frac{[A^-]}{[A^-]_o}\ \exp\left\{B_n[A^-]\right\}$$

$$\cong (c_{p,D}p_B/2)\ \exp\left\{\ln\left(\frac{[A^-]}{[A^-]_o}\right) + B_n[A^-]\right\} \qquad (6.70a')$$

If for all the time periods investigated the following relation holds,

$$B_n[A^-] >> \ln\,([A^-]/[A^-]_o) \qquad (6.71a)$$

then Equation (6.70a') can be written as

$$-\frac{d}{dt}\left\{\frac{[A^-]}{[A^-]_o}\right\} \cong (c'_{p,D}p_B/2)\ \exp\left\{B_n[A^-]\right\} \qquad (6.72a)$$

Equation (6.72a) can be integrated to give the logarithmic equation of desorption:

$$[A^-] \cong -(1/B_n)\ \ln\left\{B_n c'_{p,D}[A^-]_o\,t/2 + \exp\,(-B_n[A^-]_o)\right\} \qquad (6.73a)$$

For the case (ii), the differential equation is

$$-\frac{d[A^-]}{dt} \cong (c_{n,D}n_{1,D}/2)\,[A^-] \qquad (6.74a)$$

Integration gives

$$[A^-] \cong [A^-]_o\ \exp\left\{-c_{n,D}n_{1,D}\,t/2\right\} \qquad (6.75a)$$

From these above extreme cases we see that the desorption rate equation associated with an inversion-depletion space charge region, Equation (6.69a) can either be logarithmic or exponential depending on the relative magnitudes of $R_C(\downarrow)$ and $R_V(\downarrow)$.

For the desorption of positive adions, $[D^+]$, from a p-type semiconductor, the general results are:

$$-\frac{d}{dt}[D^+] \cong [D^+]\left\{c_{p,A}p_{1,A} + c_{n,A}n_s\right\} \qquad (6.68b)$$

which can also be written as

$$-\frac{d[D^+]}{dt} = [D^+]\left\{c_{p,A}p_{1,A} + c'_{n,A}n_B \ \exp(B_p[D^+])\right\} \qquad (6.69b)$$

where

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

when $R_C(\uparrow) >> R_V(\uparrow)$, [case (i)]

$$[D^+] \cong -(1/B_p)\ \ln\left\{B_p c'_{n,A} n_B [D^+]_o\, t + \exp(-B_p[D^+]_o)\right\} \qquad (6.73b)$$

when $R_C(\uparrow) << R_V(\downarrow)$, [case (ii)]

$$[D^+] = [D^+]_o \ \exp(-c_{p,A}p_{1,A}t) \qquad (6.75b)$$

Rate Laws of Desorption Associated With a Depletion Space Charge Region

For the desorption of negative adions from n-type semiconductors, we shall discuss the case when $u'_s < 0.9$. Under the condition of ultra-high vacuum, $[A] = 0$, and the adsorption can be neglected. Then, the situation will be the transfer of electrons mainly to the conduction band, and $R_C(\downarrow) >> R_V(\downarrow)$. Therefore the result will be the same as Equation (6.75a).

For the desorption of positive adions from p-type semiconductors, then $R_v(\uparrow) >> R_c(\uparrow)$, and the result is the same as Equation (6.75b).

DISCUSSION

In the last two sections, the rate equations for the adsorption and the desorption of charged particles on semiconductor surfaces have been derived. These equations were written in terms of atoms and atomic ions. For the adsorption or desorption of molecular ions, the corresponding rate equation can be obtained by the following replacements:

$[A^-]$ becomes $[A_n^-]$

$[A]$ becomes $[A_n]$

$[D^+]$ becomes $[D_n^+]$

$[D]$ becomes $[D_n]$

In the remainder of this section we shall point out the limitations and the special features of the derived rate equations. The electrical phenomena associated with the rate process of adsorption and desorption of charged particles shall also be discussed.

The Limitations

(1) In the derivation of the rate equations, we have applied the formulas for u'_s or u_s, which were obtained in Chapter 2 for the case of non-degenerate semiconductors. Consequently, the derived rate laws are limited to the cases contemplated in Chapter 2; that is, homogeneous, non-degenerate semiconductors.

(2) The integrated rate equations for adsorption are applicable to isobaric processes only. Otherwise only the differential rate equations should be used.

(3) The integrated rate equations for desorption are to be used in case of high vacuum or high temperature degassing. Otherwise only the differential rate equations for desorption should be used.

The Special Features

(1) The rate equations for adsorption and desorption of adions on semiconductors are derived on the monolithic basis of charge transfer theory.

(2) The form of the derived rate equations for both adsorption and desorption of charged particles are dependent on the space charge regions, i.e., the typeness of the semiconductor adsorbent.

The logarithmic rate equations for adsorption are obtained for a depletion or depletion-inversion space charge region on an extrinsic semiconductor adsorbent and for the accumulation space charge region on an intrinsic semiconductor with $u_s \mid \leqslant 0.9$.

For an accumulation space charge region on an extrinsic semiconductor or on an intrinsic semiconductor with $| u_s | > 2$, a rate equation in the form of an infinite series was obtained, e.g. Equations (6.45a, b) and (6.46a, b), instead of the simple power rate equation such as Equation (6.2). We shall discuss this in the following paragraph.

The rate equation such as Equation (6.46a) is an infinite series. It converges when $(L_m/2p_{1,A}[A])[A^-]^3 < 1$; when it is equal to 1, the rate of adsorption is zero, and the adsorption process attains dynamic equilibrium. Therefore, at any time before equilibrium, when there is a rate process, Equation (6.46a) always converges. Equation (6.46a) can be written as,

$$[A^-] + (1/4)(L_m/2p_{1,A}[A])[A^-]^4 + \ldots = [A]\, c_{p,A} p_{1,A} t \qquad (6.76)$$

The first order approximation is therefore,

$$[A^-] \cong [A]\, c_{p,A} p_{1,A} t \qquad (6.77)$$

During the adsorption $[A^-]$ increases with time. The terms with higher order of $[A^-]$ will be gradually important as $[A^-]$ increases, and the first order approximation will not be adequate. However, the series on the left hand side of Equations (6.76) can always be approximated by the form, Const $\cdot\ [A^-]^m$, for certain ranges of values of

$[A^-]$ in the neighborhood of a median value, say, $[A^-]_1$. To see this, let $g\{[A^-]\}$ represent the series on the left hand side of the Equation (6.76), and $k_B[A^-]^m$, be the approximation of the series in the neighborhood of $[A^-]_1$.

$$g_1 = k_B[A^-]_1^m \tag{6.78}$$

$$g_1' = \left(\frac{dg}{d[A^-]}\right)_{[A^-]_1} \cong m k_B[A^-]_1^{m-1} \tag{6.79}$$

Therefore $$m \cong g_1'[A^-]_1/g_1 \tag{6.80}$$

The constant k_B can be determined by combining Equations (6.80) and (6.78). The power rate equation, then, becomes:

$$k_B[A^-]^m \cong [A]\, c_{p,A} p_{1,A}\, t \tag{6.81}$$

or

$$[A^-]^m \cong [A]\, B_D t \tag{6.81a}$$

where $$B_D \equiv (c_{p,A} p_{1,A}/k_B) \tag{6.82}$$

Equation (6.80) brings out another point, namely, that the exponent "m" is a function of the median value, $[A^-]_1$, in the neighborhood of which the approximation [Equation (6.81a)] is valid. Furthermore, "m" increases as $[A^-]_1$, increases. This has been borne out by the papers of Bangham et al.(18a, b) Their data show that "m" equals 3 to 4 "initially"(18a) and 10 to 12 finally.(18b)

Electrical Phenomena Associated With the Rate Process of Adsorption and Desorption of Charged Particles

Electrical phenomena such as surface conductance and work function changes associated with surface charges due to adsorption have been analyzed and discussed in Chapters 3 and 4. These relationships can be used to check the rate equations derived in this chapter.

For example, in case of high surface ion concentration $[A^-]$, on a p-type semiconductor, it was shown in Chapter 3, that

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

In the case of adsorption at high coverage, $[A^-]$ is related with time through Equation (6.81a), therefore,

$$\Delta\sigma_s = q\mu_p \left\{ B_D [A] t \right\}^{1/m} \qquad (6.82)$$

In the case of initial desorption of $[A^-]$ from a p-type semiconductor, Equation (6.62a) can be combined with Equation (3.23) to give

$$\Delta\sigma_s = \frac{(\Delta\sigma_s)_o}{\left\{ 1 + 2[A^-]_o d_p t \right\}^{1/2}} \qquad (6.83)$$

where $(\Delta\sigma_s)_o = q\mu_p [A^-]_o$

Similarly in the case of work function, ϕ_{th}, we can use the relationships in Chapter 4. For example, in the case of acceptors on a p-type semiconductor with $u_s' > 2$, we can use Equation (4.48a) and Equation (6.81a) to obtain,

$$\Delta\phi_{th} = (2kT/m) \ \ln t + \text{const.} \qquad (6.84)$$

For acceptors on an n-type semiconductor when a depletion-inversion space charge region is generated, we can use Equations (5.71) and (6.52a) or (6.53a) to obtain

$$\Delta\phi \cong B_n kT (1/B_n) \ \ln t + Z_n$$

or

$$\Delta\phi_{th} \cong kT \ \ln t + \text{const.} \qquad (6.85)$$

Other equations relating $\Delta\phi_{th}$ and time in the rate process of adsorption and desorption can be similarly obtained.

COMPARISON WITH EXPERIMENTAL OBSERVATIONS

In this section, we shall compare the derived rate laws as well as the change of the electric properties associated with gas adsorption or desorption with observations reported in literature.

Data by Enikeev, Roginsky and Rufov

We shall first discuss the data presented by Enikeev et al,(7) which has been summarized by Equations (6.1), (6.2), and (6.3) for "accumulation adsorption", and by Equations (6.4), (6.5), and (6.6) for "depletion adsorption". The data are also represented by Figure 6.1.

For accumulation adsorption, i.e., oxygen (acceptor) on NiO (p-type), curve 2 in Figure 6.1 shows the oxygen adsorbed as a function of time, and can be represented by the Equation (6.81a), with $m = 1.7$. Curve 1 in Figure 6.1 shows the change in work function with time, and can be represented by Equation (6.84).

For depletion adsorption, i.e., oxygen (acceptor) on MnO_2 (n-type), the observed data are represented by Curve 3 in Figure 6.1 for the amount of oxygen adsorbed as a function of time. It can be explained by Equation (6.53a). The work function change during adsorption (as a function of time) was represented by Curve 4, in Figure 6.1. It bears out Equation (6.85).

Enikeev et al do not report the temperature of their measurement, but the slope of Curve 4 indicates that the temperature was approximately $345^{\circ}K$.

The fact that Curve 1 is essentially parallel to Curve 4 is at first surprising. However, the slope of Curve 1 should be $2kT/m$, where $m = 1.7$. The parallelicity of the curves then is expected as long as the measurements were made in the same temperature range.

Data by Linde

Linde(9) has reported investigations of adsorption of oxygen and other gases on Co_3O_4, Mn_3O_4, $CoMn_2O_4$ and $MnCo_2O_4$. However, only the change of electrical conductivity of $MnCo_2O_4$ during the adsorption of oxygen and CO have been studied. His data are represented by Figures 6.2 and 6.3. He reported that $MnCo_2O_4$ is a p-type semiconductor with conductivity at 20^oC of 1.5×10^{-4} mho/cm. Both oxygen and carbon monoxide are acceptors on $MnCo_2O_4$ as a function of gas up-take. Figure 6.3 presents the rate for adsorption of oxygen (acceptor) on $MnCo_2O_4$ (p-type). His data agree with those of Enikeev et al; that is, for accumulation adsorption a power rate equation of the form of Equation (6.81a) is obtained. The exponent "m" is 2.4 in Linde's system.

Data by Sebenne

More recently Sebenne(10) studied the adsorption of oxygen (acceptor) on CdS (n-type) in a doctoral thesis in solid state physics at the University of Paris. He reported that CdS is an n-type semiconductor with $E_g = 2.42$ ev., at 300^oK and dielectric constant 11.6. His data are represented by Figures 6.4 and 6.5 in its original scale.

Since Figure 6.4 shows clearly that $Y'_s > kT$, therefore his data can not be explained by the theory of Barry and Stone(8) for low surface adion concentration, which assumed that $u'_s < 0.9$. According to Equation (6.85) the slope of the straight line portion in Figure 6.4 should be about kT, ($T = 300^oK$). The rate law is represented in Figure 6.5. It beautifully bears out Equation (6.53a). The slope of the figure cannot be checked against the theories here since the surface ion concentration is not known.

Other Observations

Observations on the long time work function changes induced by light and electrostatic field have been reported by Pratt and Kolm(35) for germanium, silicon, aluminum, and gold. These authors did not measure the rate of gas adsorption or desorption. They reported that the incremental work function induced by an electrostatic field in a gaseous ambient atmosphere as measured by contact potential difference decays logarithmically after the removal of the field. The slope of the ϕ_{th} vs log t plot varies between (1/2)kT and kT for all samples with temperature range, 195° - 373°K. This can be explained on the same basis as the above explanation for Sebenne's data. However, their data on gold can not be explained on the same basis since gold probably does not form a semiconducting surface oxide. Furthermore, we have no assurance that the decay of work function is due to adsorption, nor of the condition of the surface of their sample. Therefore, we shall not emphasize their data.

Incremental conductivity due to field effect and subsequent relaxation has been reported by Lyashenko and Chernaya.(36) They reported that the current relaxation process associated with different ambients during field effect measurements can be approximated by the Becquerel hyperbolic equation. Such an equation is similar to Equation (6.83). However, these authors present no information to justify that the relaxation process is due to desorption of gases.

In a similar nature the earlier reported data on gas adsorption(1, 2) and some of the data recently reported on gas adsorption and desorption,(37) do not report the electrical properties of the solid adsorbent which was used; therefore, they can not be used to check our theory.

CONCLUSION

For the rate equations of gas adsorption, and the associated changes in the electrical properties of the semiconductor, the theory presented in this chapter has been borne out. However, there is virtually no data which could furnish enough information to check the derived rate laws for gas desorption.

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b) Bangham, D. H., W. Sever, "Experimental Investigation of the Dynamical Equation of the Process of Gas-Sorption", London Philosophical Magazine, Series 6, 49, 935-945 (1925).

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FIGURES

Fig. 6.1 Work-function variation and rate of adsorption of oxygen on NiO and MnO_2. (after Enikeev, Roginsky and Rufov).

NiO
1. $\Delta\phi_{th}\ \alpha\ \log t$
2. $\log\theta\ \alpha\ \log t$

MnO_2
3. $\theta\ \alpha\ \log t$
4. $\Delta\phi_{th}\ \alpha\ \log t$

Fig. 6.2 Change in the electrical conductivity of $MnCO_2O_4$ (p-type) caused by the adsorption of acceptors: oxygen (1), and carbon monoxide (2), at $100^{\circ}C$ (after Linde).

Fig. 6.3 The rate of adsorption of oxygen (acceptor) on $MnCO_2O_4$ (p-type) at $100^{\circ}C$ (after Linde).

Fig. 6.4 Work-function variation during adsorption of oxygen (acceptor) on CdS (n-type) at $300^{\circ}K$ as measured by contact potential difference (after Sebenne[10]).

Fig. 6.5 The rate of adsorption of oxygen (acceptor) on CdS (n-type, $n_B = 5 \times 10^{15}/cm^3$) at $300^{\circ}K$ (after Sebenne[10]).

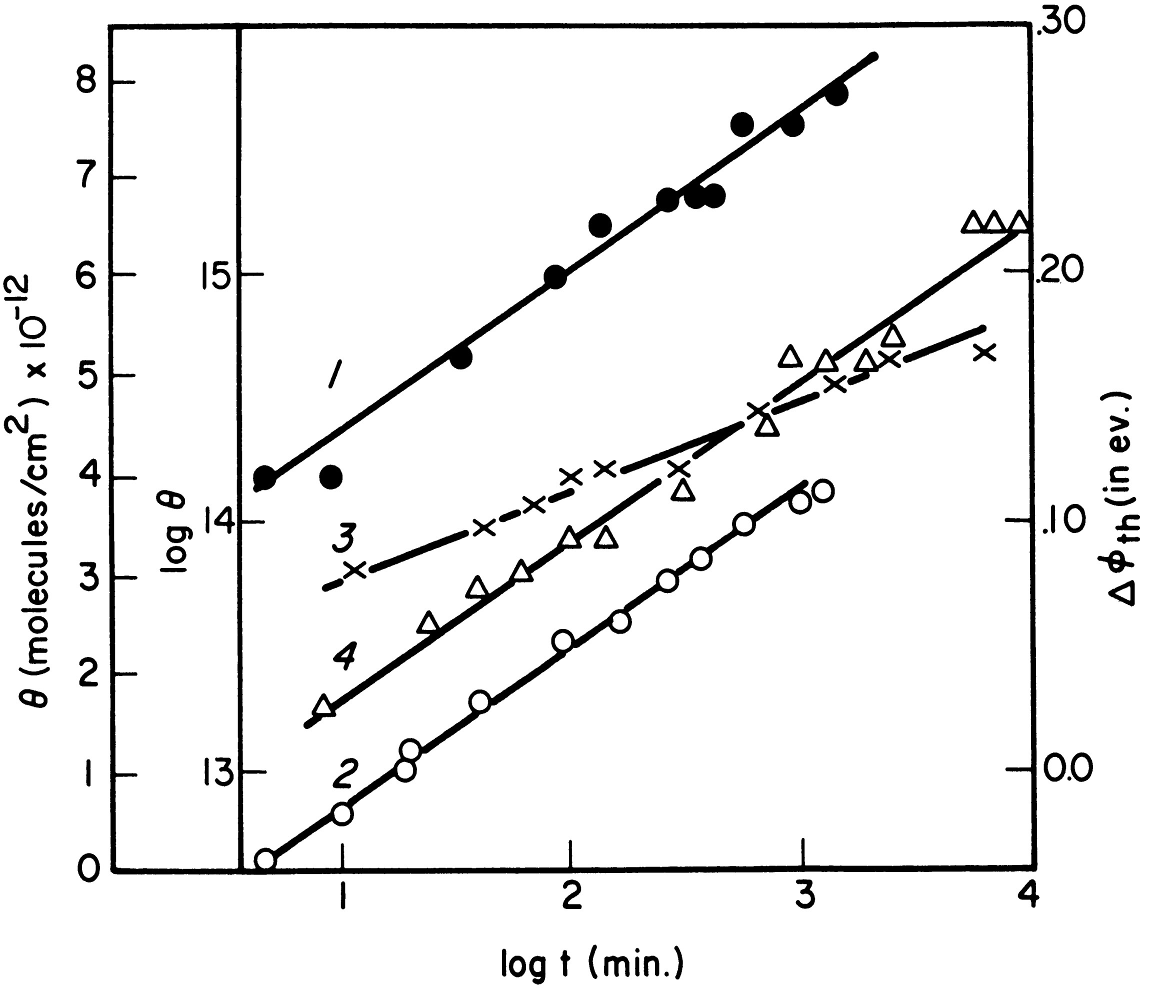

Fig. 6.1 Work-function variation and rate of adsorption of oxygen on NiO and MnO_2 (after Enikeev, Roginsky and Rufov).

NiO
1. $\Delta\phi_{th}$ α log t
2. log θ α log t

MnO_2
3. θ α log t
4. $\Delta\phi_{th}$ α log t

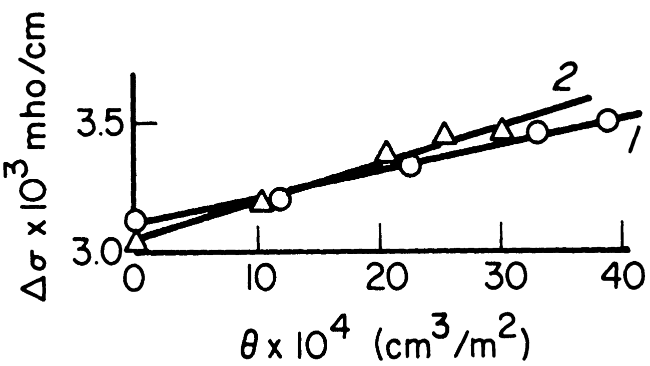

Fig. 6.2 Change in the electrical conductivity of $MnCO_2O_4$ (p-type) caused by the adsorption of acceptors: oxygen (1), and carbon monoxide (2), at 100°C (after Linde).

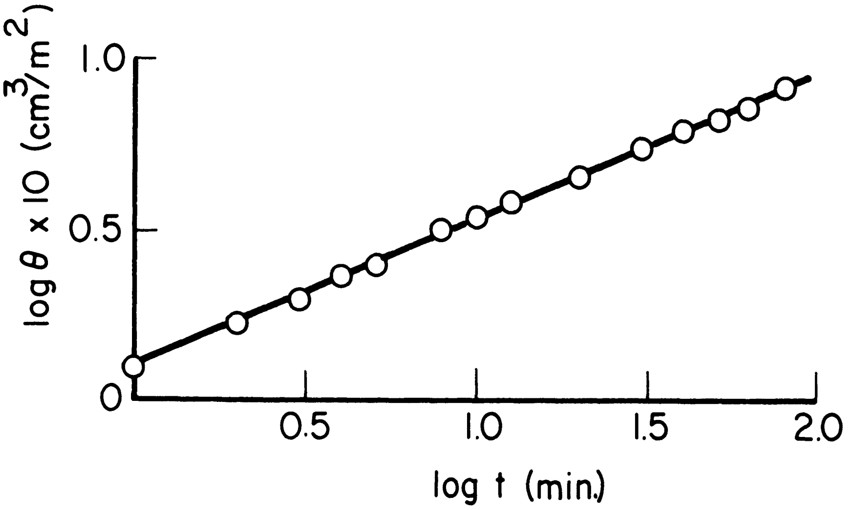

Fig. 6.3 The rate of adsorption of oxygen (acceptor) on $MnCO_2O_4$ (p-type) at 100°C (after Linde).

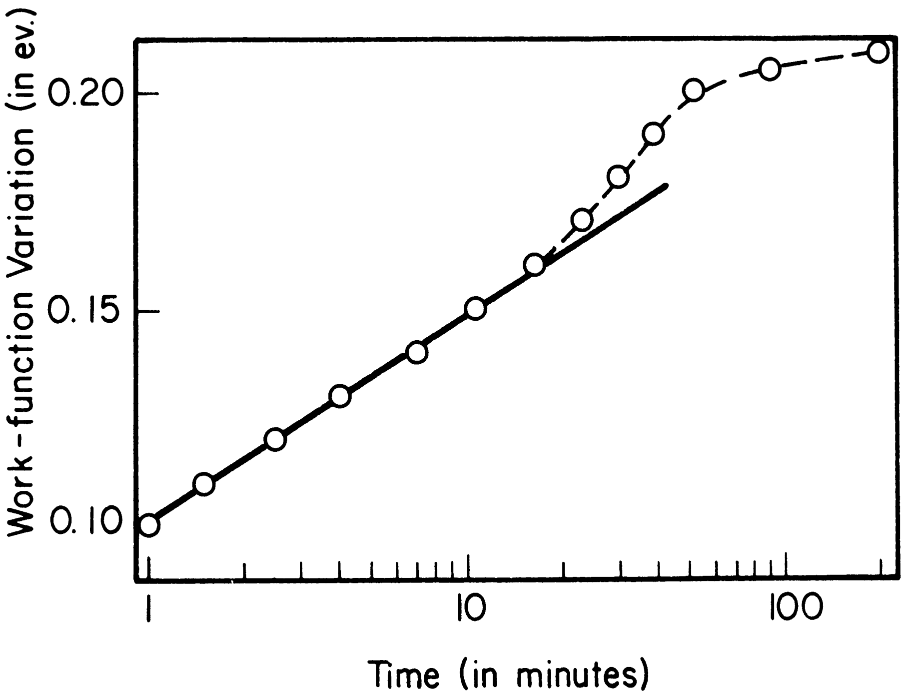

Fig. 6.4 Work-function variation during adsorption of oxygen (acceptor) on CdS (n-type) at 300°K as measured by contact potential difference (after Sebenne[10]).

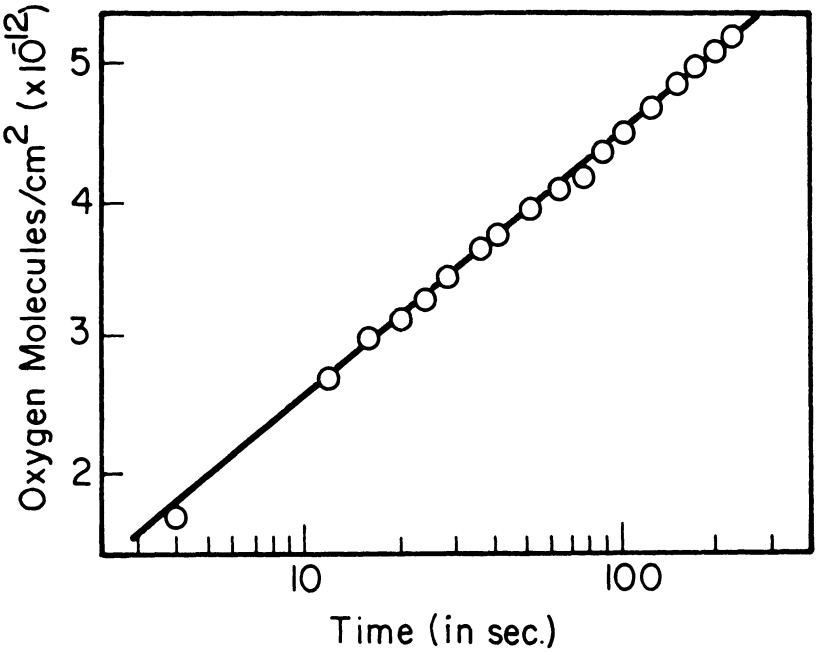

Fig. 6.5 The rate of adsorption of oxygen (acceptor) on CdS (n-type, $n_B = 5 \times 10^{15}/cm^3$) at 300°K (after Sebenne[10]).