

# The Electron Factor in the Kinetics of Chemisorption on Semiconductors

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The kinetics of chemisorption on semiconductors is investigated within the framework of the electron theory. The electrically neutral and charged forms of chemisorption are taken into account, and the kinetics of each of these forms is considered. The conditions of electron equilibrium on the surface in the process of adsorption are discussed. The activation energy of adsorption is calculated as a function of the parameters characterizing the electronic state of the system. The kinetics of desorption is considered. The nature of reversible and irreversible chemisorption is investigated.

## I. INTRODUCTION

In earlier papers on the electron theory of chemisorption and catalysis on semiconductors (1) the role of the electron factor in the kinetics of chemisorption was practically ignored. The authors limited themselves to a discussion of adsorption equilibrium. This is a "white spot" of the electron theory. Indeed, the experimenter investigating chemisorption on semiconductors is dealing, in most cases, with a kinetic process, and only very rarely with stationary adsorption equilibrium.

We observe, however, that the kinetics of chemisorption was investigated within the framework of the "boundary layer theory" (Randschichttheorie) in the theoretical papers of Hauffe and co-workers (2, 3), Germain (4), and other authors (5, 6). In all these papers (and this is characteristic of the boundary layer theory) only the charged form of chemisorption was discussed, whereas the electrically neutral form, and transitions of the chemisorbed particle from one form to another were completely ignored.

The kinetics of activated chemisorption was approached from completely similar positions in the early works of Th. Wolkenstein (7), in which the existence of "weak" bonding in chemisorption was neglected,

while the free electrons or holes on the surface were regarded as centers of adsorption (as is done in the boundary layer theory).

In the present paper the kinetics of chemisorption on semiconductors is investigated from the viewpoint of the electron theory of chemisorption. To be definite, it is assumed that the chemisorbed particles are of the acceptor type, that is, that they can exist on the surface in an electrically neutral or negatively charged state (corresponding, respectively, to "weak" and "strong" bonding to the surface), and can be converted from one state to the other.

Let

$$N^0 = N^0(t) \quad \text{and} \quad N^- = N^-(t)$$

be the surface concentrations of chemisorbed particles in the neutral and charged states, respectively, and

$$N(t) = N^0(t) + N^-(t)$$

the total number of chemisorbed particles of the given species per unit of surface at the time  $t$ . If electron equilibrium exists on the surface at the time  $t$ , then the relative amounts of the charged and neutral forms of chemisorption on the surface at this time are given by the formulas of Fermi statistics:

$$\left. \begin{aligned} \eta^-(t) &= \frac{N^-(t)}{N(t)} = \left[ 1 + \exp \frac{\epsilon_s^-(t) - v^-}{kT} \right]^{-1} \\ &= \left[ 1 + \exp \frac{v^+ - \epsilon_s^+(t)}{kT} \right]^{-1} \\ \eta^0(t) &= \frac{N^0(t)}{N(t)} = \left[ 1 + \exp \frac{v^- - \epsilon_s^-(t)}{kT} \right]^{-1} \\ &= \left[ 1 + \exp \frac{\epsilon_s^+(t) - v^+}{kT} \right]^{-1} \end{aligned} \right\} \quad (1)$$

The meaning of the symbols is clear from Fig. 1, which represents the band scheme of a semiconductor with a negatively charged surface:  $A$  is the local level of the chemisorbed particle, and  $FF$ , the Fermi level.

Denote by  $\tau$  the average lifetime of the particle in the chemisorbed state, by  $\tau^0$  and  $\tau^-$  the average lifetimes of the chemisorbed particle in the electrically neutral and charged states, respectively. It is shown in the present paper that condition (1) is approximately valid only if  $\tau \ll t$ , i.e., electron equilibrium sets in on the surface during the process of adsorption if

$$\tau^0, \tau^- \ll \tau \quad (2a)$$

whereas in the opposite limiting case of

$$\tau \ll \tau^0, \tau^- \quad (2b)$$

electron equilibrium sets in simultaneously with adsorption equilibrium. In the latter case the activation energy of adsorption depends on the electronic state of the system. Which of the two limiting cases (2a) or (2b) will take place depends on the nature of the adsorbent and the adsorbate. The kinetics of chemisorption is different in these two cases.

The kinetics of desorption (at zero pressure) is also investigated. In the case (2a) electronic equilibrium on the surface is maintained during desorption, and desorption proceeds to the end. But in the case (2b) electronic equilibrium on the surface is disturbed in the process of desorption. In the latter case desorption is only partial (partially irreversible adsorption). The relative amounts of the reversible and the irreversible forms of chemisorption depend

on the nature and the biography of the adsorbent.

## 2. FORMULATION OF THE PROBLEM

Denote by  $a_1$  and  $a_2$  the number of particles of the given species adsorbing and desorbing, respectively, per unit of time on unit surface of the semiconductor at given constant pressure  $P$  and temperature  $T$ . Let  $C_1, C_2, C_3, C_4$  be the number of electron transitions occurring in unit time on unit surface, denoted by the corresponding vertical arrows in Fig. 1. These are transitions in which the chemisorbed particle is converted from the neutral to the charged state (Transitions 1 and 4, Fig. 1) or vice versa (Transitions 2 and 3). Assuming that only particles in the neutral state are desorbed from the surface (whereas particles in the charged state do not participate in exchange with the gaseous phase) we can write down:

$$\left. \begin{aligned} (dN^0/dt) &= (a_1 - a_2) - [(C_1 - C_2) \\ &\quad - (C_3 - C_4)] \\ (dN^-/dt) &= (C_1 - C_2) - (C_3 - C_4) \end{aligned} \right\} \quad (3)$$

where

$$\left. \begin{aligned} a_1 &= \alpha_1 P (N^* - N) \\ a_2 &= \alpha_2 N^0 \exp(-q/kT) \\ C_1 &= \beta_1 n_s N^0 \\ C_2 &= \beta_2 N^- \exp(-v^-/kT) \\ C_3 &= \beta_3 p_s N^- \\ C_4 &= \beta_4 N^0 \exp(-v^+/kT) \end{aligned} \right\} \quad (4)$$

whereas

$$\left. \begin{aligned} \alpha_1 &= (2\pi M kT)^{-1/2} \kappa / N^* \\ \kappa &= \kappa_0 \exp(-E_0/kT) \end{aligned} \right\}$$

Here  $N^*$  is the surface concentration of adsorption centers, i.e., the maximum number of particles that can be adsorbed per square centimeter;  $q$ , the energy required to remove a neutral particle from the surface ("weak" binding energy);  $M$ , the mass of the adsorbed particle;  $\kappa$ , the probability of capture of a particle by the surface;  $E_0$ , the activation energy;  $n_s$ , and  $p_s$ , the concentrations of free electrons and holes, respectively, in the plane of the surface (the plane  $x = 0$  in Fig. 1). The meaning of  $v^-$  and  $v^+$  is clear from Fig. 1.

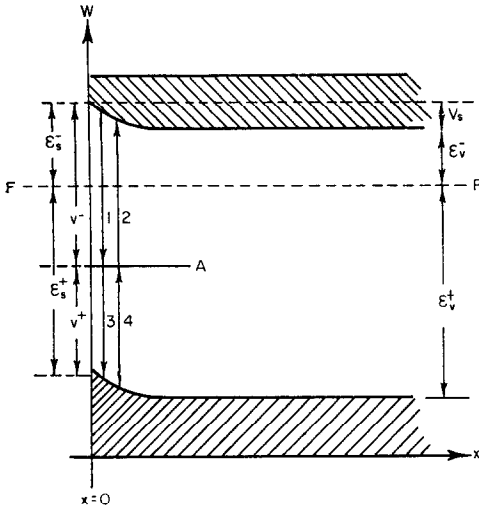


FIG. 1.

Obviously we have:

$$\left. \begin{aligned} (1/\tau) &= \alpha_2 \exp(-q/kT) \\ (1/\tau^0) &= \beta_1 n_s + \beta_4 \exp(-v^+/kT) \\ (1/\tau^-) &= \beta_3 p_s + \beta_2 \exp(-v^-/kT) \end{aligned} \right\} \quad (5)$$

Limiting ourselves for simplicity to the region of small surface coverage (Henry's region  $N \ll N^*$ ) and observing that when adsorption equilibrium is attained (i.e., at  $t = \infty$ ):

$$a_1 = a_2 \quad \text{and, hence,} \quad \alpha_1 P N^* = N_{\infty}^0 / \tau \quad (6)$$

(where  $N_{\infty}^0$  is the value of  $N^0$  at  $t = \infty$ ), we can rewrite Eq. (3) as follows:

$$\left. \begin{aligned} \frac{dN^0}{dt} &= \frac{N_{\infty}^0 - N^0}{\tau} - \left( \frac{N^0}{\tau^0} - \frac{N^-}{\tau^-} \right) \\ \frac{dN^-}{dt} &= \frac{N^0}{\tau^0} - \frac{N^-}{\tau^-} \end{aligned} \right\} \quad (7)$$

We seek the solution of this system of simultaneous equations for the initial conditions

$$N^0 = N^- = 0 \quad \text{at} \quad t = 0 \quad (8)$$

We observe [see ref. (5)] that  $1/\tau$  is the probability of desorption, while  $1/\tau^0$  and  $1/\tau^-$  are the probabilities, respectively, of charging and neutralization of a chemisorbed particle (i.e., the probabilities, respectively,

of the local level  $A$  in Fig. 1 acquiring and losing an electron) in unit time.

We shall use Boltzmann's expressions for the concentrations  $n_s$  and  $p_s$ :

$$\left. \begin{aligned} n_s &= C_n \exp(-\epsilon_s^-/kT) & \epsilon_s^- &= \epsilon_v^- + V_s \\ p_s &= C_p \exp(-\epsilon_s^+/kT) & \epsilon_s^+ &= \epsilon_v^+ - V_s \end{aligned} \right\} \quad (9)$$

We thus assume that electron equilibrium exists in the body of the semiconductor, and that the electron and hole gases are nondegenerate.

It must be observed that formulas (9) are approximate. Indeed, the process of chemisorption, in general, involves a change in the surface charge and, hence, a flow of current in the semiconductor; in other words, strictly speaking, it causes a disturbance of electron equilibrium in the body of the semiconductor. However, we shall proceed from the approximate formulas (9) (as is done in the theory of electrical conductivity or in the theory of thermionic emission), but shall take into account the variation of the terms  $\epsilon_s^-$  and  $\epsilon_s^+$  in (9) in the course of adsorption:

$$\left. \begin{aligned} \epsilon_s^- &= \epsilon_s^-(N^-) = \epsilon_v^- + V_s(N^-) \\ \epsilon_s^+ &= \epsilon_s^+(N^-) = \epsilon_v^+ - V_s(N^-) \end{aligned} \right\} \quad (10)$$

The parameters  $\tau^0$  and  $\tau^-$  in (7), in agreement with (5) and (9), should also be regarded as changing in the process of adsorption:

$$\tau^0 = \tau^0(N^-) \quad \tau^- = \tau^-(N^-)$$

We observe that in the given case of adsorption of acceptor particles we have:

$$V_s(0) \leq V_s(N^-) \leq V_s(N_{\infty}^-)$$

and, hence, according to (10) and (9):

$$\left. \begin{aligned} \epsilon_s^-(0) &\leq \epsilon_s^-(N^-) \leq \epsilon_s^-(N_{\infty}^-) \\ n_s(0) &\geq n_s(N^-) \geq n_s(N_{\infty}^-) \\ \epsilon_s^+(0) &\geq \epsilon_s^+(N^-) \geq \epsilon_s^+(N_{\infty}^-) \\ p_s(0) &\leq p_s(N^-) \leq p_s(N_{\infty}^-) \end{aligned} \right\} \quad (11)$$

At  $t = \infty$ , i.e., when adsorption equilibrium, and, simultaneously, electron equilibrium set in on the surface, we have  $dN^-/dt = 0$ , and, hence, according to (7) and (1):

$$\begin{aligned}
 (\tau^-/\tau^0) &= (N_{\infty}^-/N_{\infty}^0) = (\eta^0/\eta^-) \\
 &= \exp [(v^- - \epsilon_s^-)/kT] \\
 &= \exp [(\epsilon_s^+ - v^+)/kT] \quad (12)
 \end{aligned}$$

In the case of a sufficiently high or sufficiently low position of the Fermi level on the surface of the crystal expressions (5) for  $1/\tau^0$  and  $1/\tau^-$  are greatly simplified. Indeed, at  $t = \infty$  we have  $C_1 = C_2$  and  $C_3 = C_4$ , whence, according to (4) and (12):

$$\left. \begin{aligned}
 &\frac{\beta_1 n_s N_{\infty}^0}{\beta_4 N_{\infty}^0 \exp(-v^+/kT)} \\
 &= \frac{\beta_2 N_{\infty}^- \exp(-v^-/kT)}{\beta_4 N_{\infty}^0 \exp(-v^+/kT)} \\
 &= \frac{\beta_2}{\beta_4} \exp[(v^+ - \epsilon_s^-)/kT] \\
 &\frac{\beta_3 p_s N_{\infty}^-}{\beta_2 N_{\infty}^- \exp(-v^-/kT)} \\
 &= \frac{\beta_4 N_{\infty}^0 \exp(-v^+/kT)}{\beta_2 N_{\infty}^- \exp(-v^-/kT)} \\
 &= \frac{\beta_4}{\beta_2} \exp[(\epsilon_s^- - v^+)/kT]
 \end{aligned} \right\}$$

and, hence, on the basis of (5) (assuming that the coefficients  $\beta_2$  and  $\beta_4$  are of the same order of magnitude):

$$\left. \begin{aligned}
 (1/\tau^0) &= \beta_1 n_s \\
 (1/\tau^-) &= \beta_2 \exp(-v^-/kT) \\
 &\text{if } \exp[(\epsilon_s^- - v^+)/kT] \ll 1
 \end{aligned} \right\} \quad (13a)$$

$$\left. \begin{aligned}
 (1/\tau^-) &= \beta_3 p_s \\
 (1/\tau^0) &= \beta_4 \exp(-v^+/kT) \\
 &\text{if } \exp[(\epsilon_s^+ - v^-)/kT] \ll 1
 \end{aligned} \right\} \quad (13b)$$

We observe that if condition (13a) is satisfied at  $t = \infty$ , that is, when adsorption equilibrium is established (upon the completion of adsorption), then it is satisfied, as follows from (11), at  $0 \leq t \leq \infty$ , i.e., before adsorption begins and in the process of adsorption. We shall make use of this circumstance in what follows.

In case (13a) the valence band plays practically no part in the electron transitions; on the other hand, in case (13b) it is the conductivity band which practically drops out of the game.

### 3. KINETICS OF ADSORPTION

Let us return to the system of simultaneous equations (7). It can be solved in

general form, if we assume  $\tau^0, \tau^- = \text{const}$ . We shall proceed on this assumption. It denotes that the change in the bending of the energy bands (see Fig. 1) due to adsorption is negligibly small compared to the initial (at  $t = \infty$ ) bending of the bands due to a surface charge of nonadsorptive origin. It is evident that this condition can exist at a sufficiently high density of surface states on the original surface.

The solution of Eq. (7) on the assumption of  $\tau^0, \tau^- = \text{const}$  and for the initial conditions (8) has the form:

$$\left. \begin{aligned}
 N^0(t) &= \left\{ N_{\infty}^0 / (\tau_2 - \tau_1) \tau \right\} \\
 &\quad \cdot \left\{ \tau_2 (\tau - \tau_1) [1 \right. \\
 &\quad \left. - \exp(-t/\tau_2)] + \tau_1 (\tau_2 - \tau) \right. \\
 &\quad \left. [1 - \exp(-t/\tau_1)] \right\} \\
 N^-(t) &= \left\{ N_{\infty}^- / (\tau_2 - \tau_1) \right\} \\
 &\quad \cdot \left\{ \tau_2 [1 - \exp(-t/\tau_2)] \right. \\
 &\quad \left. - \tau_1 [1 - \exp(-t/\tau_1)] \right\}
 \end{aligned} \right\} \quad (14)$$

where

$$\left. \begin{aligned}
 (1/\tau_1) &= \lambda \{ 1 + [1 - (\mu/\lambda^2)]^{1/2} \} \\
 (1/\tau_2) &= \lambda \{ 1 - [1 - (\mu/\lambda^2)]^{1/2} \} \\
 \lambda &= \frac{1}{2} [(1/\tau^0) + (1/\tau^-) + (1/\tau)] \\
 \mu &= (1/\tau^-)(1/\tau)
 \end{aligned} \right\} \quad (15)$$

If  $\tau^0, \tau^- \ll \tau$ , or  $\tau \ll \tau^0, \tau^-$ , then  $(\mu/\lambda^2) \ll 1$ , and expressions (15) for  $1/\tau_1$  and  $1/\tau_2$  have the form:

$$\left. \begin{aligned}
 (1/\tau_1) &= 2\lambda = (1/\tau^0) + (1/\tau^-) + (1/\tau) \\
 \left( \frac{1}{\tau_2} \right) &= \frac{\mu}{2\lambda} = \frac{(1/\tau^-)(1/\tau)}{(1/\tau^0) + (1/\tau^-) + (1/\tau)}
 \end{aligned} \right\} \quad (16)$$

and, hence, in this case

$$(\tau_1/\tau_2) = (\mu/4\lambda^2) \ll 1 \quad (17)$$

The functions  $N^0 = N^0(t)$  and  $N^- = N^-(t)$  according to (14), and on the assumptions  $\tau^0, \tau^- \ll \tau$  and  $\tau \ll \tau^0, \tau^-$ , are schematically depicted in Fig. 2(a,b) and Fig. 2(c,d), respectively. Figures 2(a) and 2(c) refer to the case  $\eta^- \ll \eta^0$  (or  $\tau^- \ll \tau^0$ ), while Figs. 2(b) and 2(d), to the case  $\eta^0 \ll \eta^-$  (or  $\tau^0 \ll \tau^-$ ). We shall restrict ourselves to a discussion of these two limiting cases, which correspond to the predominance in stationary adsorption equilibrium of one of the

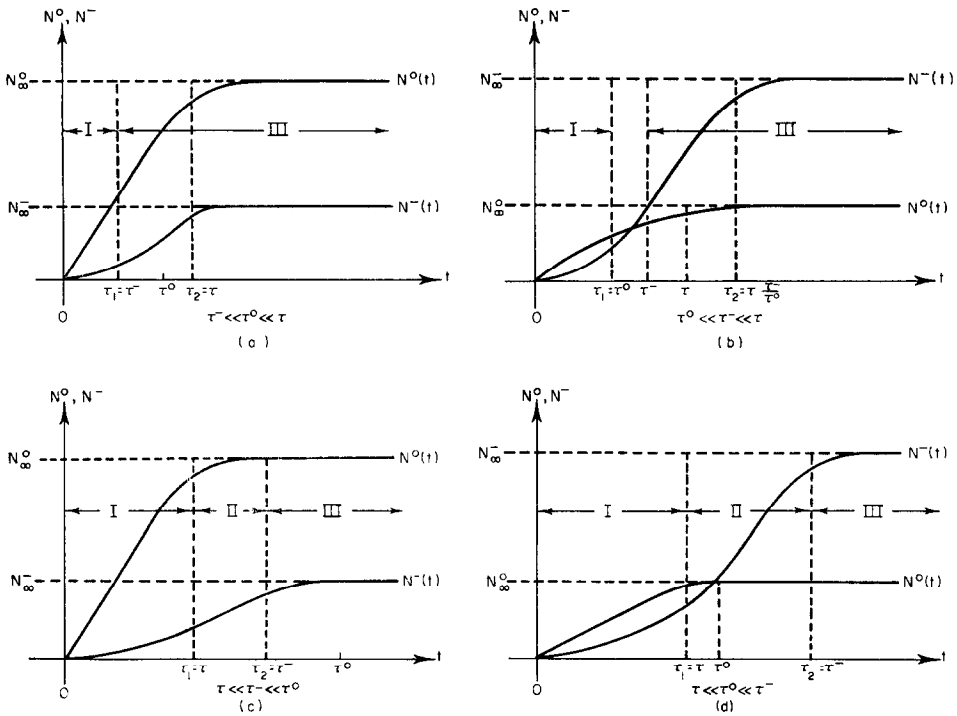


Fig. 2.

two coexisting forms of chemisorption (neutral or charged). In reality, one usually deals only with these limiting cases.

Consider Regions I, II, and III in Fig. 2.

**Region I.** First consider the region of sufficiently low surface coverage (Region I). We assume that  $t \ll \tau_1$ , where, according to (16) (see also Fig. 2),  $\tau_1$  is the least of the quantities  $\tau^0, \tau^-, \tau$ . Then, [if we also take into consideration Eq. (17)], Eq. (14) becomes:

$$\left. \begin{aligned} N^0(t) &= N_{\infty}^0 \cdot (t/\tau) \ll N_{\infty}^0 \\ N^-(t) &= N_{\infty}^- \cdot (t^2/2\tau_1\tau_2) \\ &= N_{\infty}^- \cdot (t^2/2\tau\tau^-) \ll N_{\infty}^- \end{aligned} \right\} \quad (18)$$

since, as follows from (16),

$$\tau_1\tau_2 = \tau\tau^-$$

Hence, we derive from (18), in accordance with (12):

$$(N^-/N^0) = (\eta^-/\eta^0)(t/2\tau^-) = (t/2\tau^0) \quad (19)$$

and, therefore,

$$(N^-/N^0) \ll 1, \quad \text{since} \quad t \ll \tau^0$$

i.e., in the given region of surface coverage the neutral form of chemisorption predominates on the surface.

In addition,

$$(N^-/N^0) \ll (\eta^-/\eta^0), \quad \text{since} \quad t \ll \tau^- \quad (20)$$

i.e., we are in a region far from electron equilibrium.

At  $t \ll \tau_1$  it also follows from (14), on the basis of (12):

$$\left. \begin{aligned} (dN^0/dt) &= (N_{\infty}^0/\tau) \\ (dN^-/dt) &= (N_{\infty}^-/\tau^-) \cdot (t/\tau) \\ &= (N_{\infty}^0/\tau^0) \cdot (t/\tau) \end{aligned} \right\}$$

whence, according to (6):

$$\begin{aligned} \left(\frac{dN}{dt}\right) &= \left(\frac{dN^0}{dt}\right) + \left(\frac{dN^-}{dt}\right) \\ &= \left(\frac{N_{\infty}^0}{\tau}\right) \left(1 + \frac{t}{\tau^0}\right) = \left(\frac{N_{\infty}^0}{\tau}\right) \\ &= \alpha_1 P N^* \end{aligned} \quad (21)$$

where  $\alpha_1$  has the form (4). We see that in the region under consideration adsorption takes place with an activation energy

$E_0$ , which is independent of the electron parameters.

**Region III.** Consider now Region III in Fig. 2 ( $t \gg \tau^-$ ). According to (16), in this region we have  $t \gg \tau_1$ , and hence, if we take into consideration (17), Eqs. (14) can be written in the form:

$$\begin{aligned} N^0(t) &= N_{\infty}^0 \left[ 1 - \left( \frac{\tau - \tau_1}{\tau} \right) \exp \left( -\frac{t}{\tau_2} \right) \right] \\ N^-(t) &= N_{\infty}^- \left[ 1 - \exp \left( -\frac{t}{\tau_2} \right) \right] \end{aligned} \quad (22)$$

In the case  $\tau^0, \tau^- \ll \tau$  (Fig. 2a,b) we have, according to (16)  $\tau_1 \ll \tau$  and, hence, (22) can be written in the form:

$$\begin{aligned} N^0(t) &= N_{\infty}^0 [1 - \exp(-t/\tau_2)] \\ N^-(t) &= N_{\infty}^- [1 - \exp(-t/\tau_2)] \end{aligned} \quad (23)$$

in the case  $\tau \ll \tau^0, \tau^-$  [Fig. 2(c,d)] we have, according to (16),  $\tau_1 = \tau$ , and  $\tau_2 = \tau^-$ , and, hence, from (22) we obtain:

$$N^0(t) = N_{\infty}^0 \quad N^-(t) = N_{\infty}^- \quad (24)$$

It follows from (23) and (24)

$$(N^-/N^0) = (N_{\infty}^-/N_{\infty}^0) = (\eta^-/\eta^0)$$

i.e., in the region under consideration electron equilibrium exists on the surface. We see that in the case  $\tau \ll \tau^0, \tau^-$  electron equilibrium is established only after adsorption equilibrium sets in, whereas at  $\tau^0, \tau^- \ll \tau$  it can be considered to exist at any moment of time  $t$  (at  $t \gg \tau^-$ ) throughout the process of adsorption.

In the latter case we obtain from (14), utilizing (12) and (16), for the adsorption rate:

$$\begin{aligned} \left( \frac{dN}{dt} \right) &= \left( \frac{dN^0}{dt} \right) + \left( \frac{dN^-}{dt} \right) \\ &= \left( \frac{N_{\infty}^0}{\tau_2} \right) \left( 1 + \frac{\tau^-}{\tau^0} \right) \exp \left( -\frac{t}{\tau_2} \right) \\ &= \left( \frac{N_{\infty}^0}{\tau} \right) \exp \left( -\frac{t}{\tau_2} \right) \end{aligned}$$

At  $t \ll \tau_2$  we thus arrive once more at formula (21).

**Region II.** Lastly, we discuss the intermediate Region II in Fig. 2(c,d) in which  $\tau_1 \ll t \ll \tau_2$ . Here, in accordance with (16),

$\tau_1 = \tau$ ,  $\tau_2 = \tau^-$ , and, hence, according to (17),  $\tau \ll \tau_2$ . Equations (14) can now be rewritten as follows:

$$\left. \begin{aligned} N^0(t) &= N_{\infty}^0 \tau_1 (\tau_2 - \tau) / \tau_2 \tau = N_{\infty}^0 \\ N^-(t) &= N_{\infty}^- (t/\tau^-) \ll N_{\infty}^- \end{aligned} \right\} \quad (25)$$

We see that in the given range of  $t$  the fraction of the neutral form of chemisorption remains practically constant (after reaching equilibrium value), while the fraction of the charged form increases with the time, remaining, however, far from the equilibrium value. Dividing the second of the equalities (25) by the first, we again arrive at condition (20), which denotes that we are in the region far from electron equilibrium.

Differentiating  $N^0$  and  $N^-$  in (14) with respect to  $t$ , we obtain for the region under consideration:

$$\begin{aligned} (dN^0/dt) &= (N_{\infty}^0/\tau)(\tau - \tau_1)/\tau_2 \\ (dN^-/dt) &= (N_{\infty}^-/\tau_2) \end{aligned}$$

or, taking into consideration that, according to (16) and (12):

$$\left. \begin{aligned} (\tau - \tau_1)/\tau_2 &= (\tau^2/\tau^0\tau^-)(1 + \tau^0/\tau^-) \\ &= (\tau^2/\tau^0\tau^-)(1/\eta^-) \\ (N_{\infty}^-/\tau_2) &= (N_{\infty}^-/\tau^-) = (N_{\infty}^0/\tau^0) \end{aligned} \right\}$$

we obtain

$$\begin{aligned} (dN^0/dt) &= (N_{\infty}^0/\tau^0)(\tau/\tau^-)(1/\eta^-) \\ (dN^-/dt) &= (N_{\infty}^0/\tau^0) \end{aligned}$$

and, hence (assuming to be definite,  $(\tau/\tau^-) \ll \eta^- \leq 1$ ):

$$\begin{aligned} \left( \frac{dN}{dt} \right) &= \left( \frac{dN^0}{dt} \right) + \left( \frac{dN^-}{dt} \right) \\ &= \left( \frac{N_{\infty}^0}{\tau^0} \right) \left[ \left( \frac{\tau}{\tau^-} \right) \left( \frac{1}{\eta^-} \right) + 1 \right] \\ &= \left( \frac{N_{\infty}^0}{\tau^0} \right) \end{aligned} \quad (26)$$

When the Fermi level is not too low Eq. (26), on the basis of (13a) and (9), takes the form:

$$\begin{aligned} (dN/dt) &= (dN^-/dt) = N_{\infty}^0 \beta_1 n_s \\ &= [k_0 \exp(-E/kT)]P \end{aligned} \quad (27)$$

where, according to (4) and (9):

$$E = E_0 - q + \epsilon_s^- = E_0 - q + \epsilon_v^- + V_s \quad (28)$$

We see that in the given case the activation energy of adsorption depends on the position of the Fermi level on the adsorbent surface. It thus becomes possible to change the activation energy by proper treatment of the specimen: The introduction of an acceptor impurity in the body of the semiconductor should, according to (28), lead to an increase in  $E$ , whereas a donor impurity should lead to a decrease in  $E$  (due to the increase, or, respectively, the decrease of  $\epsilon_v^-$ ); the adsorption of a foreign acceptor or donor gas should have the same effect (due to the increase, or, respectively, the decrease of  $V_s$ ).

It is also evident from (28) that there must be a one-to-one relation between the activation energy of adsorption, on the one hand, and the electrical conductivity and work function of the specimen, on the other hand. Indeed, the electron component of the conductivity decreases, and the hole component increases with the lowering of the Fermi level, i.e., with increase in  $\epsilon_v^-$ . Thus, for  $n$ -type specimens the electrical conductivity and the activation energy change in opposite sense, whereas for  $p$ -type specimens they change in the same sense (remember, we are discussing the adsorption of an acceptor gas). In all cases the work function and the activation energy change in the same sense: indeed, the work function (we are speaking of the thermionic work function) is determined up to a constant term by the quantity  $\epsilon_s^-$ .

We observe in conclusion that formula (26), which we obtained on the assumption that  $\tau^0, \tau^- = \text{const}$ , can also be deduced, as can be shown, without resorting to this assumption, i.e., in the general case  $\tau^0 = \tau^0(N^-)$ ,  $\tau^- = \tau^-(N^-)$ . If upon the establishment of adsorption equilibrium the Fermi level on the surface of the crystal is not too low [so that at  $N^- = N_\infty^-$  condition (13a) is satisfied], then formula (26) takes the form (27), while in (28) now  $V_s = V_s(N^-)$ . In the case  $\eta^0 \ll \eta^-$  [Fig. 2(d)] we can put  $N^- = N$ . We see that in this case the activation energy of chemisorption is a function of the surface coverage.

Experimental investigations of the variation of the work function with surface coverage (8) lead to the following relations:

$$V_s = AN + B \quad \text{or} \quad V_s = A' \ln N + B'$$

Inserting these relations in (28), and then in (28) and (27) and integrating, we obtain, respectively, the kinetic logarithmic isotherm and the Bangham isotherm which are frequently observed in reality. We note that these kinetic isotherms were earlier deduced theoretically in the boundary-layer theory (6,9).

#### 4. KINETICS OF DESORPTION

We consider now the kinetics of desorption. Let there be adsorption equilibrium, and also electron equilibrium on the surface at given values of  $T$  and  $P$ . Assume that at  $t = 0$  the pressure falls off sharply, after which (at  $t > 0$ ) it is kept equal to zero. We are interested in the trend of desorption with time, i.e., in the relations  $N^0 = N^0(t)$  and  $N^- = N^-(t)$  at  $t \geq 0$ .

The problem consists in solving the simultaneous equations (7), in which, according to (6), we must put  $N_\infty^0 = 0$ . The initial conditions have the form

$$N^0 = N_0^0, \quad N^- = N_0^- \quad \text{at} \quad t = 0 \quad (29)$$

where  $N_0^0$  and  $N_0^-$  satisfy the condition [compare with (12)]:

$$(N_0^-/N_0^0) = (\tau^-/\tau^0) = (\eta^-/\eta^0) \quad (30)$$

Assuming  $\tau^0, \tau^- = \text{const}$ , i.e., assuming that the bending of the bands remains practically constant in the course of desorption (this assumption will be justified later on), we obtain:

$$\left. \begin{aligned} N^0(t) &= [N_0^0/(\tau_2 - \tau_1)\tau][\tau_2(\tau - \tau_1) \\ &\quad \cdot \exp(-t/\tau_2) + \tau_1(\tau_2 - \tau) \\ &\quad \cdot \exp(-t/\tau_1)] \\ N^-(t) &= [N_0^-/(\tau_2 - \tau_1)][\tau_2 \\ &\quad \cdot \exp(-t/\tau_2) - \tau_1 \exp(-t/\tau_1)] \end{aligned} \right\} \quad (31)$$

whence:

$$N(t) = [N_0/(\tau_2 - \tau_1)\tau][\tau_2(\tau - \eta^0\tau_1) \cdot \exp(-t/\tau_2) + \tau_1(\eta^0\tau_2 - \tau) \cdot \exp(-t/\tau_1)] \quad (32)$$

where we denote

$$N_0 = N(0)$$

As in Section 3, we shall only discuss the two limiting cases:  $\tau^0, \tau^- \ll \tau$  and  $\tau \ll \tau^0, \tau^-$ . Here  $\tau_1$  and  $\tau_2$  have the form (16), while  $\tau_1 \ll \tau_2$  and hence, at all  $t$ :

$$\tau_2 \exp(-t/\tau_2) \gg \tau_1 \exp(-t/\tau_1)$$

so that the second of Eqs. (31) has the form:

$$N^-(t) = N_0^- \exp(-t/\tau_2)$$

and therefore,

$$\begin{aligned} (N^0/N^-) &= (\eta^0/\eta^-)(1/\tau) \{ (\tau - \tau_1) \\ &\quad + (\tau_2 - \tau)(\tau_1/\tau_2) \\ &\quad \exp[-(\tau_2 - \tau_1)t/\tau_1\tau_2] \} \end{aligned} \quad (33)$$

Consider the case  $\tau^0, \tau^- \ll \tau$ . In this case, according to (16)

$$\left. \begin{aligned} \tau_1 &= \tau^0\tau^-/(\tau^0 + \tau^-) = \tau^0\eta^- = \tau^-\eta^0 \\ \tau - \tau_1 &= \tau[1 - \eta^-(\tau^0/\tau)] = \tau \\ \tau_2 &= \tau(\tau^0 + \tau^-)/\tau^0 = \tau/\eta^0 \\ \tau_2 - \tau &= \tau[1 - (1/\eta^0)] = \tau(\tau^-/\tau^0) \end{aligned} \right\} \quad (34)$$

and Eqs. (32) and (33), on the basis of (34), can be written as follows:

$$\begin{aligned} N(t) &= N_0 \exp(-t/\tau) \\ (N^0/N^-) &= (\eta^0/\eta^-) \end{aligned}$$

We see that in this case electron equilibrium on the surface is maintained in the course of desorption. In other words, the relative amounts of the charged and neutral forms of chemisorption on the surface do not change, but retain the values they had before desorption began.

Consider another limiting case:  $\tau \ll \tau^0, \tau^-$ . In this case, according to (16)

$$\left. \begin{aligned} \tau_1 &= \tau, \quad \tau - \tau_1 = \tau[(\tau/\tau^0) + (\tau/\tau^-)] \\ &= (\tau^2/\tau^-\eta^0) = (\tau^2/\tau^0\eta^-) \\ \tau_2 &= \tau^-, \quad \tau_2 - \tau = \tau^- \end{aligned} \right\} \quad (35)$$

and Eqs. (32) and (33), on the basis of (35), can be written

$$N(t) = N_0[\eta^0 \exp(-t/\tau) + \eta^- \exp(-t/\tau^-)] \quad (36)$$

$$(N^0/N^-) = (\eta^0/\eta^-) \{ (\tau/\tau^0) + (\tau/\tau^-) + \exp[-(\tau^- - \tau)t/\tau\tau^-] \} \quad (37)$$

We observe that Eq. (37) can be rewritten as follows:

$$\begin{aligned} (N^0/N^-) &= (\eta^0/\eta^-) \exp[-(\tau^- - \tau) \left. \begin{aligned} &t/\tau\tau^- \\ &\text{at } t \ll t^* \end{aligned} \right\} \\ (N^0/N^-) &= (\eta^0/\eta^-) [(\tau/\tau^0) + (\tau/\tau^-)] \left. \begin{aligned} &\text{at } t^* \ll t \end{aligned} \right\} \end{aligned} \quad (38)$$

where

$$\begin{aligned} t^* &= -\tau \ln [(\tau/\tau^0) + (\tau/\tau^-)] \\ &= -\tau \ln (\tau/\tau^-\eta^0) \end{aligned}$$

We see [see Eq. (38)] that desorption disturbs electron equilibrium on the surface. At  $t \ll t^*$  we move rapidly away from equilibrium as  $t$  increases, due to the fact that the relative amount of the neutral form of chemisorption on the surface decreases faster than that of the charged form. At  $t^* \ll t$  the relative amounts of the neutral and charged forms of chemisorption become constant (independent of the time) with the latter form greatly predominating (in comparison with the equilibrium value).

We see also [see Eq. (36)] that the curve  $N = N(t)$  results from the superposition of two branches: one falling off rapidly, and the other slowly [the first and second terms in (36), respectively]. If we observe desorption during a time interval, small compared with  $\tau^-$  (i.e., if  $\tau^-$  is greater than the duration of the experiment), then we can assume  $t \ll \tau^-$  in (36) and rewrite that equation as follows (see Fig. 3):

$$N(t) = N_0[\eta^0 \exp(-t/\tau) + \eta^-]$$

i.e., only a fraction  $(N_0 - N_0\eta^-) = N_0\eta^0 = N_0^0$  of the total amount of adsorbed particles  $N_0$  is desorbed, whereas the remaining

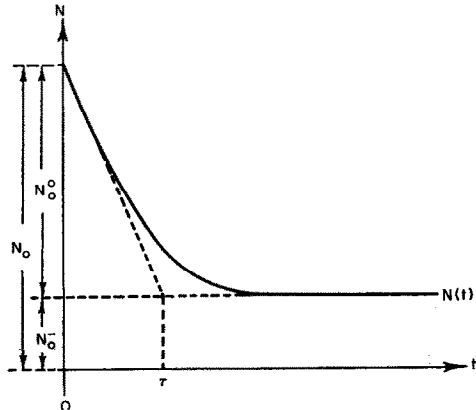


FIG. 3.



fraction  $N_0\eta^- = N_0^-$  is irreversibly bound to the surface. We are thus dealing with partially irreversible adsorption, a phenomenon frequently observed in reality, for which we can write [see Eq. (12)]:

$$\begin{aligned} (N_0^-/N_0^0) &= (\eta^-/\eta^0) = \exp [(v^- - \epsilon_s^-)/kT] \\ &= \exp [(\epsilon_s^+ - v^+)/kT] \quad (39) \end{aligned}$$

i.e., the relative amounts of the irreversible and reversible forms of chemisorption on the surface are determined, all other conditions being equal, by the position of the Fermi level, i.e., by the state of the system as a whole. We can thus regulate the ratio (39) to some extent by subjecting the adsorbent to the proper treatment (introduction of an acceptor or a donor impurity, adsorption of a foreign acceptor or donor gas).

We observe that as long as the second term in (36) remains constant, i.e., as long as  $t \ll \tau^-$ , the original assumption  $\tau^0, \tau^- = \text{const}$  can be regarded as automatically valid, regardless of the state of the surface, since only the electrically neutral form of chemisorption is removed from the surface in desorption, and, hence, the surface charge and the subsurface bending of the energy bands remain constant in the process of desorption. For the same reason a change in the work function during desorption can occur only as the result of a change in its dipole component (the contribution of the neutral form of chemisorption to the work function). We thus have a way of estimating the dipole component in the experimentally determined value of the work function.

In conclusion we estimate the values of the parameters  $\tau, \tau^0, \tau^-$  figuring in the theory. We can write (10-13):

$$\begin{aligned} \alpha_2 &= 10^{16} \text{ sec}^{-1} \\ \beta_1, \beta_3 &= 10^{-9} \text{ cm}^3 \text{ sec}^{-1} \\ \beta_2, \beta_4 &= 10^{10} \text{ sec}^{-1} \end{aligned}$$

and, hence, according to (5):

$$\left. \begin{aligned} (1/\tau) &= 10^{16} \exp(-q/kT) \\ (1/\tau^0) &= 10^{-9}n_s + 10^{10} \\ &\quad \exp(-v^+/kT) \\ (1/\tau^-) &= 10^{-9}p_s + 10^{10} \\ &\quad \exp(-v^-/kT) \end{aligned} \right\} \quad (40)$$

Putting

$$\begin{aligned} q &= 0.1 \div 2.0 \text{ ev} \\ n_s, p_s &= 10^4 \div 10^{18} \text{ cm}^{-3} \\ v^-, v^+ &= 0.1 \div 3.0 \text{ ev} \end{aligned}$$

we obtain in agreement with (40), (at  $kT = 0.04 \text{ ev}$ ):

$$\left. \begin{aligned} \tau &= 10^{-15} \div 10^4 \text{ sec} \\ \tau^0, \tau^- &= 10^{-9} \div 10^5 \text{ sec} \end{aligned} \right\}$$

We see that the values of  $\tau, \tau^0, \tau^-$  can vary within wide limits. Depending on the nature of the semiconductor and the gas, either of the two limiting cases discussed can occur:  $\tau^0, \tau^- \ll \tau$  or  $\tau \ll \tau^0, \tau^-$ . It may also happen that the Region I in Fig. 2 will be beyond the range of experimental observation. The same may apply, in other cases, to Region III.

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