

Electrons and Holes as Energy-Transport Agents in Catalysis on Semiconductors—Part I

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Received July 28, 1969

This paper presents a novel model of catalysis at semiconductor surfaces. The central postulate is that energy for catalyzing a surface reaction is provided by means of electron-hole pair production in the semiconductor and annihilation during the surface reaction. The process is analogous to electrolysis taking place at steady states apart from thermal equilibrium. Analytical results deduced from the model satisfactorily explain experimental facts which could not be accounted for by previous models of the electronic theory of catalysis.

INTRODUCTION

The evolution of the electronic theory of catalysis began more than half a century ago. A great number of the important empirical observations and theoretical interpretations in the literature, before and including 1960, were documented in the book, *The Electronic Theory of Catalysis on Semiconductors* (1). The fundamental hypothesis of the theory is that all heterogeneously catalyzed chemical reactions are either acceptor reactions or donor reactions. An acceptor reaction is catalyzed by free electrons; therefore, the activity of a semiconductor catalyst increases as its Fermi level rises relative to the mid-band energy level, E_i . In other words, for acceptor (donor)* reactions, the catalytic activity of a semiconductor mirrors its electron (hole) concentrations.

The theory was capable of explaining many empirical correlations on the covariance of catalytic activity and conductivity or electron work function of extrinsic semiconductors. However, there exist also experimental facts and empirical correlations

which are either totally unexplainable by or even contradictory to the electronic theory of catalysis. These are briefly described in the following:

(I) In the studies of N_2O decomposition over a series of catalysts prepared from a base semiconductor, reports in the literature indicated that the most active catalyst has the smallest activation energy and the lowest order of reaction (2-3).

(II) There exists a correlation between the catalytic activity of a semiconductor and the width of its forbidden zone, E_g , i.e., catalytic activity decreases as E_g increases. This correlation, unexplainable by the electron theory of catalysis, was corroborated by a total of twenty-three semiconductors for three test reactions in the temperature range 50-320°C (4-7). Its importance was reemphasized by Roginskii in a recent paper: "The authors believe that this result is not incidental and that it may be of great importance for the understanding of the mechanism of catalysis by semiconductors and the laws governing catalysis section (8)."

(III) For a series of catalyst samples prepared from a base semiconductor by doping with donors (acceptors), the catalytic activity of the sample does not always

*The parenthetical expression in this paper gives an equivalent case, e.g., for donor reaction here.

mirror its electron (hole) concentration as claimed by the electronic theory of catalysis. On the contrary, the catalyst sample possessing the maximum catalytic activity is the one having neither the highest nor the lowest electron (hole) concentration (2, 3, 9-11). Contradiction to the electronic theory of catalysis is distinctively accentuated by the hydrogen-deuterium exchange reaction over germanium catalysts. The intrinsic germanium was of an order of magnitude more active than either *n*-type or *p*-type germanium at 150°C (10). Moreover, the *n*- and *p*-types of germanium have about equal activity for the H₂-D₂ exchange reaction, as is the case of *n*- and *p*-GaAs in the dehydrogenation of isopropyl alcohol (7).

An attempt was made to explain the aforementioned empirical correlations in a paper by the author and D. R. Mason (12). The latter charge-transfer theory was a synthesis and refinement of a series of contributions in the field of catalysis. Among the earlier contributors are Pisarzhevskii, Nyrop, Wagner, Hauffe, Garner *et al.*, Roginskii, Boudart, Aigrain *et al.*, Weisz, Schwab, Wolkenstein, Garrett, and many others (1, 12-22). The scope of the charge-transfer theory is limited to chemical reactions which react via adionic intermediates at a semiconductor surface. Two charge-transfer steps with or without adionic migration and reaction steps are postulated during catalysis. The paper was successful in deriving the order of reactions for simple systems and in the interpretation of the correlation (I): the concurrence of the minimum activation energy and the lowest order of reaction. Furthermore, it anticipated the existence of electrodynamic field effects in heterogeneous catalysis. These are confirmed by recent experiments reported in the literature (3, 23-25). However, the charge-transfer theory did not give a quantitative treatment nor an analytical explanation for the aforementioned empirical correlations (II) and (III).

This paper presents a quantitative explanation for both the unaccountable empirical correlations of catalysis at semiconductor surfaces, as well as others which

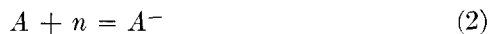
were accountable from the electronic theory of catalysis. The analysis is based on a model in which energy for catalyzing a surface reaction is transported from the semiconductor via electron-hole pair production in it and annihilation in the process of surface reactions. According to this model, catalysis at semiconductor surface is analogous to electrolysis.

A CHARGE-TRANSFER MODEL

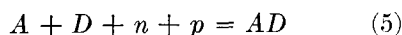
Recent experiments by Morrison and Freund (26) on the catalytic role of holes and electrons suggested the following model of charge-transfer catalysis at semiconductor surfaces: acceptors accept electrons from the conduction energy bands; donors donate electrons to the holes in the valence band. In other words, electrons and holes transfer to the adsorbed acceptor and donor states via, respectively, the conduction energy band and the valence energy band of the semiconductor catalyst. For some chemical reactions, there are both positive and negative adions among the reaction-intermediates. These positive and negative adions are generated by charge-transfer between the catalyst and the adsorbed donor and acceptor reactants, respectively. For chemical reactions involving only positive or only negative adions, there are also donors and acceptors in the adsorbed state. However, in these cases, the donors or the acceptors may be adions.

The following example illustrates the electron-hole pair production and the roles of electrons, *n*, and holes, *p*, in surface reactions. Let *A* and *D* denote the adsorbed acceptor and donor states, respectively; *AD* denotes the product of the reaction.

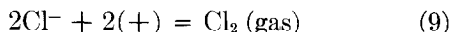
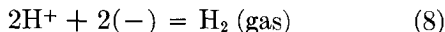
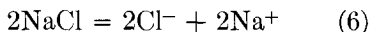
$$\Delta H = n + p \text{ (in semiconductor)} \quad (1)$$



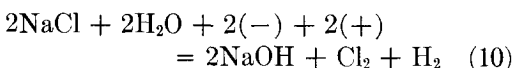
where ΔH is the energy required for electron-hole pair production in the semiconductor. The overall reaction of reactions (2)-(4) is:



That is, for every AD molecule produced, an electron-hole pair is annihilated. The process is analogous to electrolysis of NaCl in aqueous media, *e.g.*,



where $(-)$ and $(+)$ denote charges from cathode and anode respectively. The overall reaction is:



One observes from reactions (5) and (10) the corresponding roles played by n and $(-)$ and by p and $(+)$ in the respective reaction. It is well understood in electrolysis that the activation energy, as well as chemical energy for reaction (10), are supplied by the external electric power. Analogously, it is inferred that the activation energy and chemical energy, if needed, for reaction (5) are supplied by the electron-hole pairs. Hence, during catalysis, there is a net rate of energy transfer from the interior of the catalyst to the intermediates through electron-hole pair production and annihilation. But, there is *no net rate* of charge-transfer between the catalyst and the reaction intermediates. The electron-hole pairs are produced in the

interior of the semiconductor-catalyst by photo excitation in photocatalysis (11, 26) and by thermal excitation in ordinary heterogeneous catalysis.

For continuous transformation and transportation of energy by the semiconductor via electron-hole pair production and annihilation during catalysis, the catalyst-reactant system must be at a state apart from the thermodynamic equilibrium. A slight deviation of states between the surface and the interior of the catalyst is necessary for a net transfer of electrons and holes from the interior of a semiconductor to the reaction intermediates at its surface. Hence, instead of one Fermi energy level, E_f , for both electrons and holes at an equilibrium state there are two quasi Fermi levels, F_n and F_p , for electrons and holes in the steady state of catalysis via electron-hole recombinations (27-28). Furthermore, in the case of ordinary catalysis, the energy level of the acceptor, E_a , must be located higher than, or coincide with, the energy level of the donor, E_d . These are illustrated in Fig. 1. However, it is not necessary to postulate that E_a and E_d are single valued as shown. For photo-catalysis by the postulated charge-transfer model, the case $E_d > E_a$ is possible at temperatures such that the adsorbed donors and acceptors can not thermally emit electrons into the conduction band and holes into the valence band, respectively. This will be

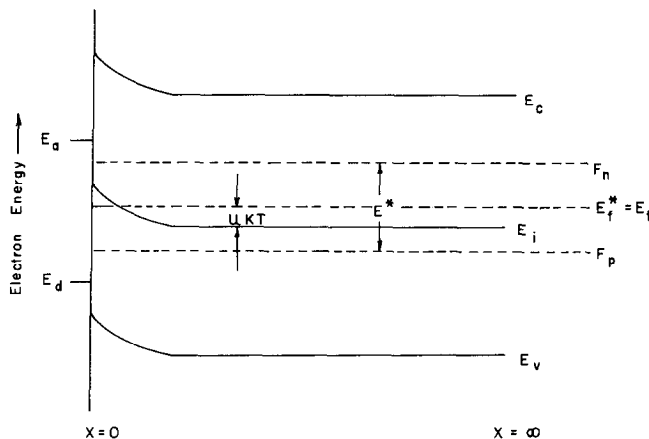


FIG. 1. Energy band diagram for a semiconductor with a positive space charge layer. It illustrates energy levels at steady states apart from thermal equilibrium during catalysis.

discussed again in connection with the data in (11).

The physics of the model is similar to the one discussed and treated by Brattain and Bardeen for electron-hole recombination via two types of surface traps: donors and acceptors (28). However, there is one essential difference: the two types of surface traps in Brattain and Bardeen's model act in parallelism for electron-hole recombination with no net chemistry between the traps. But in our model, the adsorbed donor and acceptor act in series through surface reactions for electron-hole recombination. New chemicals are produced when one or more electron-hole pairs are annihilated via the surface reactions involving the donors and acceptors.

QUANTITATIVE ANALYSIS

Analytical treatment of the rates of chemical reactions according to the charge-transfer model of the last section is presented in this section. Two types of reactions are treated separately in each of the two subsections, A and B. The type of reactions as represented by (2)–(5) is treated in subsection A. In this type of reactions, electron-hole pair recombination is accomplished through surface adionic reaction. The second type of reactions, treated in subsection B, involves the formation of new acceptors or donors by a surface reaction step. The initial step is the adsorption of acceptors (donors) followed by electron (hole) capture from the semiconductor. Electron-hole pair recombination is achieved by the formation of a new adionic donor (acceptor) state which captures holes (electrons) from the semiconductor (the reverse situation is given in parentheses).

The basic semiconductor physics applied in the analysis can be found in many standard references, as are the notations (29). For completeness, a list of symbols is given in the appendix.

Reactions (2)–(5) are used as model reactions in our analysis. This case is considered in subsection A. Other reactions concerned in this paper, N_2O decomposition

and C_3H_7OH dehydrogenation, are considered in subsection B.

1. Subsection A: Reactions (2)–(5)

According to Reactions (2) and (3), the net rate of electron transfer and that of hole transfer are, respectively:

$$U_n = K_n[(n_s^* \langle A \rangle^* - n_1 \langle A^- \rangle^*)]. \quad (11)$$

$$U_p = K_p[(p_s^* \langle D \rangle^* - p_1 \langle D^+ \rangle^*)]. \quad (12)$$

At thermodynamic equilibrium, variables with asterisks are replaced by their counterpart without asterisks. $\langle A \rangle$ and $\langle A^- \rangle$; $\langle D \rangle$ and $\langle D^+ \rangle$ are related by:

$$f(E_a) \equiv \frac{\langle A^- \rangle}{\langle A \rangle + \langle A^- \rangle} = \frac{1}{1 + \exp(E_a - E_t)/kT}, \quad (13)$$

$$f(E_d) \equiv \frac{\langle D \rangle}{\langle D^+ \rangle + \langle D \rangle} = \frac{1}{1 + \exp(E_d - E_t)/kT}, \quad (14)$$

where $f(E)$ is the Fermi distribution function of an effective energy level E . Substituting the equilibrium values of the asterisk-variables into Eqs. (11) and (12), one obtains:

$$U_n = U_p = 0. \quad (15)$$

Equation (15) means that at thermodynamic equilibrium, there is no net transfer of electrons and of holes. Hence, catalysis via electron-hole recombination must occur at a steady state apart from thermodynamic equilibrium.

During catalysis, the rate of electron-hole annihilation is equal to the rate of the surface adionic combination. The latter rate is identical to the rate of production of AD molecule, if the reaction is irreversible. This is assumed to be so; hence,

$$U = K \langle A^- \rangle^* \cdot \langle D^+ \rangle^* = \frac{d}{dt} (AD). \quad (16)$$

The condition of steady state is:

$$U = U_n = U_p. \quad (17)$$

Eliminating $\langle A^- \rangle$ and $\langle D^+ \rangle^*$ from Eqs. (11)–(12), (16)–(17), one obtains:

$$U^2 - U \cdot [(K_n K_p n_1 p_1 / K) + (K_n n_s^* \langle A \rangle^*) + (K_p p_s^* \langle D \rangle^*)] + K_n K_p n_s^* p_s^* \langle A \rangle^* \cdot \langle D \rangle^* = 0. \quad (18)$$

There are two roots for U in Eq. (18). The smaller of the two roots determines the rate process of chemical reaction via charge-transfer and surface adionic reaction. Two cases (a) and (b), are discussed in the sequel.

(a). Charge-transfer rate limiting. The charge-transfer rate limiting process implies that surface adionic combination is fast. It means that the rate constant K approaches infinity mathematically. Hence, from Eq. (18), one obtains:

$$U^2 - U \cdot [(K_n \cdot n_s^* \langle A \rangle^*) + (K_p \cdot p_s^* \langle D \rangle^*)] + (K_n n_s^* \langle A \rangle^*) \cdot (K_p \cdot p_s^* \langle D \rangle^*) = 0. \quad (19)$$

The two roots of Eq. (19) are:

$$U_1 = K_n \cdot n_s^* \cdot \langle A \rangle^* \quad (20)$$

and

$$U_2 = K_p \cdot p_s^* \cdot \langle D \rangle^*. \quad (21)$$

U_1 and U_2 are the *net rate* of electron transfer into the acceptor state and that of hole transfer into the donor state. It is interesting to note from Eqs. (11) and (12) and reactions (2) and (3), that U_1 and U_2 are simply the irreversible rates of electron and hole transfer. It is a direct consequence of allowing K to be infinite, i.e., assuming the reaction (4) to be very fast. The principle that the rate limiting slow step is always irreversible is manifested by Eqs. (20) and (21). This will be applied to other reactions which do not have a step corresponding to reaction (4) in subsection B.

Between U_1 and U_2 , the smaller one is the rate determining step. Hence, the actual rate of charge-transfer, U , is:

$$U = \begin{cases} U_1, & \text{if } U_1 < U_2 \\ U_2, & \text{if } U_1 > U_2 \end{cases} \quad (22)$$

Obviously, when the two charge-transfer rates, U_1 and U_2 , are equal, U has its optimum value, U_0 . From Eqs. (20) and (21), one obtains:

$$U_0 = (K_n K_p)^{1/2} (\langle D \rangle^* \langle A \rangle^*)^{1/2} n_1^*. \quad (23)$$

U_0 can be used to transform Eq. (22) into a dimensionless expression. Thus, from Eqs. (20), (21), and (23), Eq. (22) becomes:

$$(U/U_0) = \begin{cases} \exp(u_s^* - u_0^*), & \text{for } u_s^* < u_0^* \\ \exp(u_0^* - u_s^*), & \text{for } u_s^* > u_0^*, \end{cases} \quad (24)$$

where u_0^* is defined by:

$$u_0^* \equiv \ln(K_p \langle D \rangle^* / K_n \langle A \rangle^*)^{1/2}. \quad (25)$$

For small deviations from thermal equilibrium, or for intrinsic semiconductors, it can be easily shown that:

$$E_t^* = \frac{1}{2}(F_n + F_p) = E_t. \quad (26)$$

To prove Eq. (26), let us consider:

$$(n^*/n) \cdot (p/p^*) = \exp(F_n + F_p - 2E_t) / kT \quad (27)$$

since

$$n^* = n + \delta n \quad (28)$$

$$p^* = p + \delta p \quad (29)$$

where δn , δp are the perturbations of electron and hole concentrations. From Eqs. (28)–(29), one obtains:

$$F_n + F_p - 2E_t = KT \ln \left(\left(1 + \frac{\delta n}{n} \right) / \left(1 + \frac{\delta p}{p} \right) \right). \quad (30)$$

The right hand side of Eq. (30) reduces to zero when $(\delta n/n)$ and $(\delta p/p)$ are equal to one another, or when both are much less than one. Under these conditions, equation (24) becomes:

$$(U/U_0) \begin{cases} = \exp(u_s - u_0^*), & \text{for } u_s < u_0^* \\ \exp(u_0^* - u_s), & \text{for } u_s > u_0^*. \end{cases} \quad (31)$$

The significance of Eq. (31) will be discussed in connection with the previously mentioned experimental observations (III).

(b). Surface reaction rate limiting. For the case that reaction (4) is the slow step, the surface reaction constant K has a very small value. Equation (18) can now be approximated by:

$$U^2 - (K_n K_p n_1 p_1 / K) U + K_n K_p n_s^* p_s^* \langle A \rangle^* \langle D \rangle^* = 0. \quad (32)$$

Equation (18) is of the form: $U^2 - (\alpha + \beta)U + \alpha\beta = 0$. The smaller of the two roots of Eq. (18) is the desired root of Eq. (32). This can be obtained by omitting U^2 and solving for U : e.g., if $\alpha \gg \beta$, then $\beta \cong \alpha\beta/(\alpha + \beta)$. Hence, from Eq. (18), one obtains the desired root of Eq. (32),

$$U = K \cdot n_s^* \cdot p_s^* \cdot \langle A \rangle^* \cdot \langle D \rangle^* / n_1 p_1 \quad (33)$$

Since

$$n_s^* \cdot p_s^* = (n_i^*)^2 = n_i^2 \exp(F_n - F_p)/kT \quad (34)$$

and

$$n_1 \cdot p_1 = n_i^2 \exp(E_d - E_a)/kT, \quad (35)$$

Eq. (33) can be simplified to:

$$U = K \cdot \langle A \rangle^* \cdot \langle D \rangle^* \exp - [(E_d - E_a) - E^*]/kT. \quad (36)$$

Equation (36) can also be derived by introducing the physical assumption that $\langle A \rangle^*$, $\langle A^- \rangle^*$, and $\langle D \rangle^*$, $\langle D^+ \rangle^*$, are, respectively, in quasi-equilibrium, with respect to electrons and holes in the semiconductor due to the slowness of reaction (4). Hence, analogous to Eqs. (13) and (14), one now has:

$$\frac{\langle A^- \rangle^*}{\langle A \rangle^* + \langle A^- \rangle^*} = \frac{1}{1 + \exp(E_a - F_n)/kT} \quad (37)$$

and

$$\frac{\langle D \rangle^*}{\langle D^+ \rangle^* + \langle D \rangle^*} = \frac{1}{1 + \exp(E_d - F_p)/kT}. \quad (38)$$

Solving for $\langle A^- \rangle^*$ and $\langle D^+ \rangle^*$ from Eqs. (37) and (38), respectively, one obtains:

$$\langle A^- \rangle^* = \langle A \rangle^* \exp(F_n - E_a)/kT \quad (39)$$

and

$$\langle D^+ \rangle^* = \langle D \rangle^* \exp(E_d - F_p)/kT. \quad (40)$$

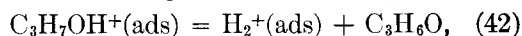
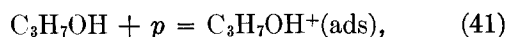
Equation (36) is now obtained by substituting $\langle A^- \rangle^*$ and $\langle D^+ \rangle^*$ from Eqs. (39) and (40), respectively, into Eq. (16).

Two points of great significance are derived from Eq. (36). Firstly, it has clearly

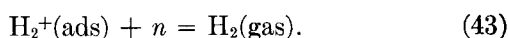
been shown that the activation energy for reaction (5) has been lowered ($F_n - F_p = E^*$), as compared to that at thermal equilibrium, due to the electron and the hole transfer into the acceptors and donors. Hence, electrons and holes may be viewed as activation energy transport agents in catalysis. Secondly, Eq. (36) shows that the rate of reaction (5) is independent of carrier concentrations of a semiconductor, if reaction (4) is the slow step. Consequently, catalysis by charge-transfer *does not always imply* a covariance of catalytic activity and carrier concentration of a semiconductor.

2. Subsection B: Electron-Hole Recombination via New States Formation and Charge-Transfer

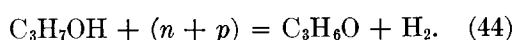
The following two hypothetical reaction-mechanisms illustrate the formation of new states. The first example is the dehydrogenation of isopropyl alcohol, in which an acceptor is formed:



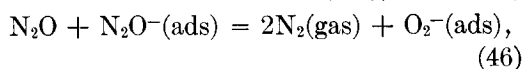
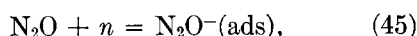
and



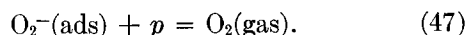
The over-all reaction is



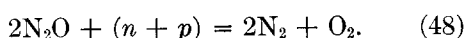
The second example is the decomposition of N_2O , in which a donor is formed:



and



The over-all reaction is



In the above examples, if reactions (42) and (46) are fast steps, the rate limiting steps are either the electron or hole transfer. The rate equations for the charge-transfer steps are obtained by applying

the aforementioned principle: the rate limiting slow step is always irreversible.

For reactions (41) and (43), the hole and electron transfer rates are given by Eqs. (21) and (20) after the following replacement:

$$\langle A \rangle^* = \langle \text{H}_2^+ \rangle^* \quad (49)$$

and

$$\langle D \rangle^* = \langle \text{C}_3\text{H}_7\text{OH} \rangle^*. \quad (50)$$

Similarly, for reactions (45) and (47), one has the following relationship:

$$\langle A \rangle^* = \langle \text{N}_2\text{O} \rangle^* \quad (51)$$

and

$$\langle D \rangle^* = \langle \text{O}_2^- \rangle^*. \quad (52)$$

Therefore, if the surface reaction step is sufficiently fast, the rate of electron-hole pair recombination for the cases in subsection B is again given by Eq. (31). Further treatment is not needed. In the remainder of this subsection, reactions (42) and (46) are considered to be slow.

By the principle that a rate limiting reaction is always irreversible, one obtains the rate equations for reactions (42) and (46):

$$U = K_d \langle \text{C}_3\text{H}_7\text{OH}^+ \rangle^* \quad (53)$$

and

$$U = K_a \langle \text{N}_2\text{O}^- \rangle^* \cdot \langle \text{N}_2\text{O} \rangle^*. \quad (54)$$

By relationships similar to Eqs. (37) and (38) and algebraic simplification, Eqs. (53) and (54) can be simplified to

$$U = K_d \langle D \rangle^* \exp(-u_s^*) \cdot \exp \left[- (E_i - E_d - E^*/2)/kT \right] \quad (55)$$

and

$$U = K_a \langle A \rangle^{*2} \cdot \exp(u_s^*) \cdot \exp \left[- (E_a - E_i - E^*/2)/kT \right]. \quad (56)$$

Two things of significance are noted in Eqs. (55) and (56). The first is the decrease of activation energy by $E^*/2$. The second is that rates of surface reactions are functions of u_s^* , which is equal to u_s for a steady state which has a small departure from the equilibrium state. Since u_s is a function of $\langle D \rangle^*$ or $\langle A \rangle^*$ through $\langle D^+ \rangle^*$ or

$\langle A^- \rangle^*$, the order of reaction for both (55) and (56) varies according to whether an accumulation, a depletion, or an inversion space-charge layer is generated underneath the surface during charge-transfer catalysis. For example, when an accumulation space-charge layer is created during catalysis, Eqs. (55) and (56) become:

$$U \propto \langle D \rangle^{*1/3} \exp(E_d - E_i + E^*/2)/kT \quad (57)$$

and

$$U \propto \langle A \rangle^{*4/3} \exp(E_i - E_a + E^*/2)kT. \quad (58)$$

Other cases may be similarly obtained by means of the relationships between u_s and the surface charge in the literature (30).

COMPARISON WITH EMPIRICAL CORRELATIONS

The aforementioned empirical correlation (I) was interpreted in Ref. (12). The empirical correlations (II), (III), and the covariance of catalytic activity and conductivity or electron work-function will be compared with our model and the analytical results derived.

1. Empirical Correlation (II): Catalytic Activity Increases as E_g Decreases

According to our model, the rate limiting processes in the phase of the semiconductor-catalyst may be either the rate of production of electron-hole pairs, or the rate of transportation of electrons and holes through the space-charge layer underneath the surface and their capture by the reaction intermediates. The production of electron-hole pairs, reaction (1), as the rate limiting process is demonstrated by the reported photocatalysis on Cu_2O and ZnO , which have little catalytic activity in the absence of illumination (11, 26). It appears that the empirical correlation (II) might also be explained, if thermal excitation of electron-hole pairs is the rate limiting step. But it is difficult to see how the catalytic activity of a semiconductor-catalyst can be dependent on the type of semiconductor (7). However, the range of temperatures at which catalysis is carried out often lies in the range of intrinsic con-

duction (7). Hence, it must be explained from charge-transfer processes.

For dehydrogenation of isopropyl alcohol, using Eqs. (49), (50), (23), and (24), one can easily obtain the effective activation energy, ΔE , for the reaction,

$$\Delta E = \frac{1}{2}(E_g - E^*) + (u_0^* - u_s^*) \cdot kT \quad \text{for } u_0^* > u_s^*, \quad (59)$$

$$\Delta E = \frac{1}{2}(E_g - E^*) + (u_s^* - u_0^*) \cdot kT \quad \text{for } u_s^* > u_0^*, \quad (60)$$

and

$$\Delta E = \frac{1}{2}(E_g - E^*) \quad \text{for } u_0^* \cong u_s^*. \quad (61)$$

From Eqs. (59)–(61), if everything else is equal, or if $E_g/2$ is of predominant magnitude over the other terms, the activation energy increases, hence the catalytic activity decreases, as E_g increases.

2. Empirical Observations (III)

Test reactions for this group of experimental observations are nitrous oxide decomposition, hydrogen-deuterium exchange, oxidative ammonolysis of propylene, and carbon monoxide oxidation. From reaction (48), the rate of N_2O decomposition is re-

lated to the rate of electron-hole recombination U by:

$$-\frac{d}{dt}(N_2O) = 2U. \quad (62)$$

For the H_2 - D_2 exchange in an equal molar mixture, and low concentrations of HD, the acceptor and donor states are given by:

$$\langle A \rangle^* = \langle H_2^+ \rangle^* + \langle D_2^+ \rangle^* + \langle HD^+ \rangle^* \quad (63)$$

and

$$\langle D \rangle^* = \langle H_2^+ \rangle^* + \langle D_2^+ \rangle^*. \quad (64)$$

The actual rate of HD production is:

$$\frac{d}{dt}(HD) = U/2. \quad (65)$$

In view of Eqs. (16), (62), and (65), one can generalize by saying that the rate of a chemical reaction, R , is proportional to U , the electron-hole recombination rate. Thus, one has

$$R = \epsilon U, \quad (66)$$

where ϵ is proportionality constant, referred to as the quantum efficiency in photocatalysis. Hence, U is a measure of the catalytic activity of a catalyst.

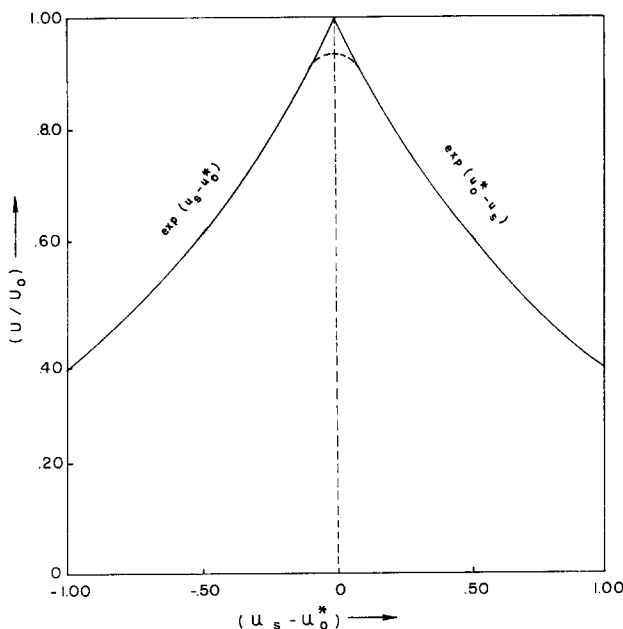


FIG. 2. A schematic plot of Eq. (30). The dashed line illustrates the case that at $u_s = u_0^*$, the rate limiting step is surface reaction.

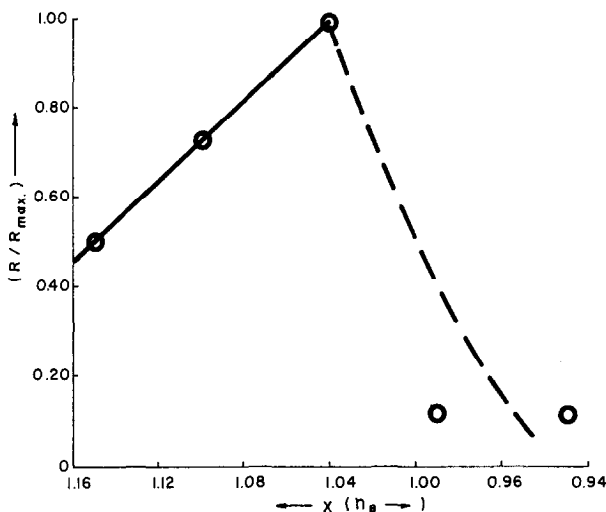


FIG. 3. Variation of catalytic activity at 300°C with catalyst composition, data from Ref. (3).

To compare with the group of empirical observations (III), Eq. (31) is plotted as the solid curve in Fig. 2. The dashed portion in the figure is for the case where surface reaction is the rate limiting step. The latter occurs under the condition that the reaction is carried out at sufficiently low temperatures and that u_s is in the neighborhood of u_0^* .

The solid Fig. 2, *i.e.*, the plot of (U/U_0) versus $(u_s - u_0^*)$, has two significant features: two branches and a sharp joint at $(U/U_0) = 1$. This is fortunate because u_s was difficult to measure during reaction. No measurement was reported in the literature. However, u_s is related $u_B = u(\infty)$ by the following relation:

$$u_s = u_B + v_s, \quad (67)$$

where $v_s = v(0)$, the dimensionless surface electrostatic potential is due to charge transfer adsorption. u_B is related to the bulk electron and hole concentrations, n_B , p_B , by:

$$u_B = \ln(n_B/n_i) = -\ln(p_B/n_i). \quad (68)$$

In turn, n_B and p_B are functions of the donor and the acceptor concentrations in the bulk of the semiconductor, respectively.

The data plotted in Fig. 3 were reported by Kim and Squires (3). The ordinate represents the rate of N_2O decomposition, (N_2O decomposed in 3 hr/m² of surface

area). The abscissa represents bulk acceptor and donor concentrations, ($x > 1$; $x < 1$), in cobalt ferrite, respectively. It is plotted such that electron concentration, and therefore u_B , increases from left to right. Upon inspection of Fig. 3, one observes the two significant above-mentioned features: two branches and a sharp joint at $R = R_{max}$, *i.e.*, $U/U_0 = 1$.

In Fig. 4 there is a plot of the data reported by Gel'bshtein *et al.* (9). The ordinate represents the rate constant of the over-all conversion of propene to acrylonitrile and acrolein. The rate of reaction, and hence, U , is proportional to this rate constant. The abscissa represents the electron work function, ϕ , of the bismuth-molybdenum oxide catalysts. ϕ is measured at 400°C in air, but not during catalysis. ϕ is related to u_s (in air) by the following:

$$\begin{aligned} \phi &= E_0 - E_f \\ &= (E_0 - E_i) - u_s. \end{aligned} \quad (69)$$

Hence, u_s (in air) increases as ϕ decreases; so is the u_B of the $MoO_3Bi_2O_3$ catalyst system. ϕ is plotted in Fig. 4, decreasing from left to right, in order that u_B increases from left to right. Once again we notice that the rate constant, G , versus ϕ plot has two branches and a sharp joint at $G = G_{max}$, (*i.e.*, $U/U_0 = 1$). However, unlike Fig. 2, the G versus ϕ plot is not symmetric. This

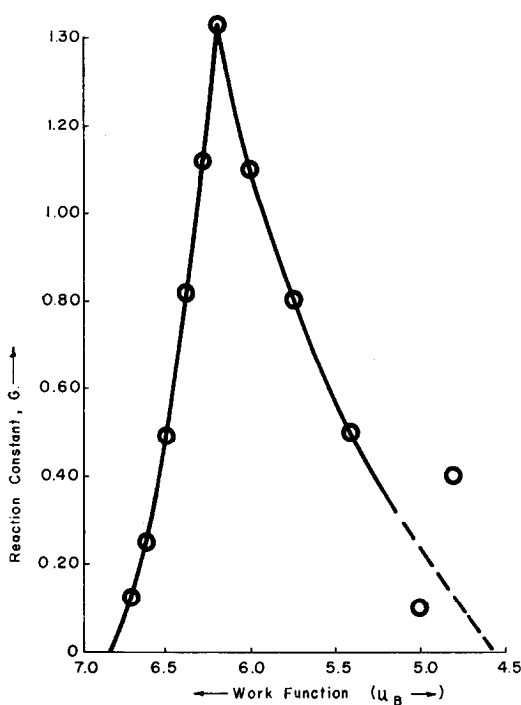


FIG. 4. Variation of rate constant, G , with the electron work function, ϕ , of $\text{MoO}_3\text{-Bi}_2\text{O}_3$ catalysts, data from Ref. (9).

may be due to the fact that v_s in Eq. (67) is not invariant as u_B varies.

Ritchey and Calvert reported, thirteen years ago, on the "Photosensitized Oxidation of Carbon Monoxide on Cuprous Oxide" (11). The reaction was carried out at $25 \pm 2^\circ\text{C}$ and at a pressure of 100–400 mm Hg. At a given light intensity, the rate of CO oxidation is dependent on the bulk concentrations of the dopants: sulfur and antimony. It was established by resistance measurements that sulfur and antimony were acceptors and donors in Cu_2O , respectively. Their data were presented in a plot [Ref. (11), Fig. 1], which exactly corresponds to Fig. 3 in this paper. The plot has these characteristics: two branches and a sharp joint at the maximum rate of reaction.

In addition, reference (11) has provided direct evidence that the rate of the chemical reaction is directly related to the rate of electron-hole pair production, reaction (1), by photo excitation. This was manifested by the experimental facts:

(1) The light used for Cu_2O sensitization has a quantum energy of 3 to 5 electron volts, ($4100 > \lambda > 2500 \text{ \AA}$), which is sufficient to excite electron-hole pairs in Cu_2O , which has an energy band gap of about 2 ev. (31).

(2) The rate of CO oxidation increased as the light intensities were increased; and the rate of the electron-hole pair production in Cu_2O is directly proportional to the intensity of light with quantum energy larger than 2 ev.!

Finally, equation (31) can be used to explain the empirical observation that an n -type and a p -type semiconductors have about the same catalytic activity, whereas, an intrinsic semiconductor has the highest activity (7, 10). By Eq. (31), the catalyst sample possessing maximum activity has a u_s , satisfying

$$u_s = u_0^* \quad (70)$$

Through Eq. (67), the dimensionless bulk potential u_B is related to u_s . Since u_0^* is a parameter pertaining to the adsorbed states and v_s is the dimensionless electrostatic potential, *a priori*, there are three possible cases in nature:

$$(i) \quad u_B = u_0^* - v_s = 0$$

$$(ii) \quad u_B = u_0^* - v_s > 0$$

and

$$(iii) \quad u_B = u_0^* - v_s < 0. \quad (71)$$

These cases (i), (ii), and (iii) of Eq. (71) imply that the catalyst having maximum activity can be either an intrinsic, an n -type, or a p -type semiconductor, respectively. References (7) and (10) manifest case (i).

3. Short Range Correlations

The covariance of catalytic activity and the conductivity or the typeness of semiconductors were explained in the literature of the electronic theory of catalysis (1). These can also be interpreted as short range correlation, i.e., the left hand and right hand branches, L.H.B. and R.H.B., of the plot in Fig. 2. On L.H.B., the catalytic activity of a semiconductor increases as

its electron concentration increases. On R.H.B., the catalytic activity of a semiconductor increases as its hole concentration increases. Furthermore, it is evident from Fig. (2) that the covariance of catalytic activity and electric conductivity can be either symbatic or antibatic, depending on the location of the maximum of (U/U_0) given by Eq. (71). It is immaterial whether the reaction intermediate is initially a donor, an acceptor, or both with respect to the semiconductor.

CONCLUSION

The novel model of charge-transfer catalysis at semiconductor surfaces is justifiable on two counts. First, the empirical correlations, unaccountable from the electronic theory of catalysis, are explained by the analytical results derived from the model. Second, the covariance of catalytic activity and semiconductivity or the type-ness of a semiconductor, on which the electronic theory of catalysis was built, are also explained and shown to be short range correlations. *A fortiori*, direct evidence also is provided by Ref. (11). However, other models of charge-transfer at semiconductor surfaces are also possible. These models will be considered in subsequent publications.

ACKNOWLEDGMENTS

The writer is indebted to Dr. S. Roy Morrison for stimulating discussions and hospitality during the author's visit to The Stanford Research Institute, Menlo Park, California. He wishes also to acknowledge the partial financial support of this work by the National Science Foundation.

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APPENDIX

A list of Principal Symbols

- $\langle A \rangle, \langle A \rangle^*$ = equilibrium and steady state surface concentrations of acceptors
- $\langle A^- \rangle, \langle A^- \rangle^*$ = equilibrium and steady state surface concentrations of "filled" acceptors
- $\langle D \rangle, \langle D \rangle^*$ = equilibrium and steady state surface concentrations of donors
- $\langle D^+ \rangle, \langle D^+ \rangle^*$ = equilibrium and steady state surface concentration of "empty" donors
- $E^* \equiv F_n - F_p$, width of E_f splitting
- $E_c = E_c(x)$, energy at lowest state of conduction band at x (from the surface)
- E_f = Fermi energy at thermodynamic equilibrium
- $E_f^* \equiv 1/2 (F_n + F_p)$, steady state mean Fermi energy
- E_g = energy gap = $E_c - E_v$
- $E_i = E_i(x)$, midband energy of the energy gap at x
- E_0 = Vacuum Energy level.
- $E_v = E_v(x)$, energy of highest state of valence band at x
- F_n = quasi Fermi energy for electrons at steady state
- F_p = quasi Fermi energy for holes at steady state for $m_n = m_p$
- G = rate constant
- k = Boltzmann constant
- K = surface reaction constant
- K_a, K_d = surface reaction constants
- K_n = capture probabilities of electrons by acceptors
- K_p = capture probabilities of holes by donor
- $n = n_i \exp(u)$
- $n = N_c \exp(E_f - E_c)/kT$, electron concentration
- $n^* = n_i \exp(F_n - E_i)/kT$
- $n^* = N_c \exp(F_n - E_c)/kT$, n at steady state
- $n_i = (N_c N_v)^{1/2} \exp(-E_g/2kT)$, intrinsic carrier concentration
- $n_i^* = n_i \exp(F_n - F_p)/2kT$, n_i at steady state
- $n_i^* = n_i \exp(F_n - F_p)/2kT$
- $n_s, p_s = n(o), p(o)$, respectively
- $n_1 = N_c \exp(E_n - E_c)/kT$
- $N_c = 2(2\pi m_n kT/h^2)^{3/2}$; m_n is electron mass, h is Plank's constant
- $N_v = 2(2\pi m_p kT/h^2)^{3/2}$, m_p is hole mass
- $p = n_i \exp(-u)$
- $p = N_v \exp(E_v - G_f)/kT$, hole concentration
- $p^* = n_i \exp(E_i - F_p)/kT$
- $p^* = N_v \exp(E_v - F_p)/kT$, p at steady state
- $p^* = n_i \exp(E_i - F_p)/kT$
- $p_1 = N_v \exp(E_v - E_d)/kT$
- T = absolute temperature
- $u = u(x) \equiv [E_f - E_i(x)]/kT$
- $u^* = u^*(x) \equiv [E_f^* - E_i(x)]/kT$
- $U = U_n = U_p$ at the steady state
- U_n = rate of electron transfer from semiconductor to acceptors
- U_0 = maximum U
- U_p = rate of hole transfer from semiconductor to donors
- $v = v(x) \equiv E_i(\infty) - E_i(x)/kT$
- ΔE = effective activation energy
- ΔH = optical or thermal energy for electron-hole pair production
- ϵ = quantum efficiency
- $\phi = E_0 - E_f$, electron work function