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THE ELECTRONIC FACTOR IN THE KINETICS OF CHEMISORPTION ON SEMICONDUCTORS

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I. REVIEW OF PUBLISHED EXPERIMENTAL WORK

1. Kinetic Laws

The physical and chemical properties of semiconductor surfaces, so important in semiconductor technology and in catalysis, are controlled essentially by chemisorption processes taking place on the surface. For this reason, the study of chemisorption on semiconductors has attracted a great deal of interest.

In order to clarify the fundamental mechanism of chemisorption, it is important to investigate the kinetics of the process. The basic characteristic is the variation of the amount adsorbed q with time t at constant temperature:

the kinetic isotherm $q = q(t)$. Kinetic isotherms are established under two types of experimental conditions: at constant pressure and at constant volume.

Usually, adsorption is fast at the very beginning of the chemisorption process (during the first minute, say), and the kinetics have been inadequately investigated in this region because of the experimental difficulties involved. This stage is followed by a slower one, whose kinetics are usually measured and reported as chemisorption kinetics. However, the chemical interaction between a gas and an adsorbent, whose initial stage is studied in chemisorption, is not confined to this stage. Chemisorption, particularly at high temperatures, can be followed by processes which affect the bulk of the adsorbent: e.g. penetration of adsorbed species into the bulk of the adsorbent, diffusion of metal in stoichiometric excess (in the case of oxide or sulphide semiconductors) from the bulk phase to the surface. In the chemisorption of oxygen on oxides this process is equivalent to growth of the crystal lattice of the adsorbent. Thus, it is important to distinguish, in experimental studies of chemisorption, between chemisorption proper and subsequent stages of sorption. This has not always been done.

The kinetics of the majority of chemisorption processes are described by the Roginskii–Zel'dovich equation[1,2]

$$dq/dt = a \exp(-\alpha q), \tag{1a}$$

where a and α are constants ($a > 0$, $\alpha > 0$). In its integrated form the equation is

$$q(t) = (1/\alpha) \ln(1 + t/t_0), \tag{1b}$$

where $t_0 = 1/a\alpha$.

Eqn. (1) was used by Roginskii and Zel'dovich[3] to describe the kinetics of the chemisorption of CO on MnO_2. Taylor and Thon[4] showed that the equation could be applied to a large number of experimental results. The constants a and α are determined as follows. One chooses a value of t_0 such that the plot of q against $\ln(1 + t/t_0)$ is linear, and from the slope of this plot α is obtained. Knowing α and t_0, we can then arrive at the value of a. We can see from Eqn. (1a) that a corresponds to the initial rate of adsorption: $a = (dq/dt)_{t=0}$. However, if we determine the initial rate of adsorption from the amount of material adsorbed during the first unit of time (i.e. as rapidly as possible after the onset of adsorption), we obtain a value much greater than a found from Eqn. (1b). This is evidence for the existence of a fast initial stage of chemisorption.

The constants a and α depend on T and P as follows: (1) on raising T, α decreases, but a, on the other hand, increases with an activation energy of about 10 kcal mole^{-1}; (2) at constant T, α tends to increase slightly as P decreases, and a increases approximately as $P^{0.8}$. Taylor and Thon conclude that in the slow stage of chemisorption described by Eqn. (1) the kinetics are relatively insensitive to the mass-action effect of the gas, and are determined mainly by changes taking place in the adsorbent.

The Table, reproduced from Stone's book, illustrates the application of Eqn. (1) to chemisorption processes, but does not claim to be comprehensive.

It should be noted that Eqn. (1) formally describes any process in which the height of the potential barrier opposing a change in some quantity is linearly related to the change in that quantity. Thus Eqn. (1) could describe not only the chemisorption stage but also any subsequent absorption stage, although it does not follow that in a kinetic isotherm consisting of two intersecting Roginskii–Zel'dovich straight lines of different slope the second line necessarily denotes some process other than chemisorption.

TABLE. Chemisorption processes conforming to the Roginskii–Zel'dovich equation.

Gas	Adsorbent	Gas	Adsorbent
H_2	Cr_2O_3	CO	MnO_2
	$ZnO \cdot Cr_2O_3$		NiO
	$\alpha MnO \cdot Cr_2O_3$	O_2	$CaO \cdot Cr_2O_3$
	ZnO		NiO
	NiO		CoO

Chemisorption involving the adsorption of more than one layer, and conforming to Eqn. (1), has been observed[5-7] in the adsorption of oxygen on thin films of oxides deposited on the appropriate metal. Engell and Hauffe[8] quote an example of the penetration of oxygen into the NiO lattice, conforming to Eqn. (1), after a chemisorption stage described by the same equation but with a different slope. Parravano and Boudart have pointed out[9] that processes such as bulk and surface diffusion can also follow a logarithmic law. It follows that a wide variety of mechanisms of gas absorption can remain concealed in Eqn. (1).

Although many chemisorption processes are described by the Roginskii–Zel'dovich equation, cases are known in which chemisorption proceeds according to some other kinetic law. Thus, Enikeev and coworkers[10-13] have shown that, when the electron work function of the adsorbent is logarithmically related to the coverage of the surface, a power law is obtained:

$$dq/dt = aq^b, \tag{2a}$$

where a and b are constants ($a > 0$, $b > 0$), or alternatively

$$q(t) = a't^{b'}. \tag{2b}$$

Examples of this behaviour include O_2 on NiO, C_3H_7OH on ZnO, and O_2 on ZnO containing Li_2O. Eqn. (2b) is called the Bangham equation, and has been used by Bangham and coworkers[14,15] to describe the adsorption kinetics of CO_2 and NH_3 on glass.

Thuillier[16] observed, in his study of the chemisorption of oxygen on ZnO, a rate process conforming to the equation

$$dq/dt = a \exp(-\alpha q^2) \tag{3}$$

(a and α constant), which had been put forward by Aigrain and Dugas[17] and Germain[18]. According to Roland and Schuttler[19], Eqn. (3) also describes the kinetics of oxygen chemisorption on TiO_2 (rutile).

2. Reversibility and Irreversibility of Adsorption

Even the earliest studies of chemisorption had revealed the existence of different forms of the bond between the chemisorbate and the surface of the adsorbent. It was found that the whole adsorbate could not always be removed completely from the surface if desorption was carried out at the same temperature as adsorption. Higher desorption temperatures increase the amount of adsorbate removed from the surface, but occasionally the species which is desorbed beyond a certain temperature is not the same as

that which had been adsorbed. This was observed by Garner and Kingman[20,21] during their study of the adsorption of hydrogen and carbon monoxide on $ZnO.Cr_2O_3$. These workers concluded that two types of adsorption are possible on oxides: "reversible" adsorption, when the adsorbate can be desorbed in its original chemical form, and "irreversible" adsorption, when the opposite is true. However, the measured heats of adsorption, which were found to lie in the range of 10–30 kcal mole^{-1}, show that even in the case of "reversible" chemisorption we are dealing with chemical rather than physical adsorption.

The presence of two forms of chemisorption was later demonstrated by many workers. The two forms are often termed the weak and the strong form of chemisorption. The relative amounts of the two forms under comparable conditions depend on the temperature at which adsorption is allowed to proceed. Thus, hydrogen adsorbed on zinc oxide below 100° is readily desorbed, whereas at temperatures higher than 100° strong adsorption is observed[22]. The adsorption of hydrogen on ZnO was studied also by Keier and Roginskii[23,24], who found that above 100° an appreciable fraction of the hydrogen is strongly adsorbed and can only be removed from the surface in the form of water by heating the specimen above 500°. The adsorption of carbon monoxide on ZnO shows similar features: several workers[25-27] found that CO which has been adsorbed at room temperature can be desorbed unchanged, whereas above 150° the adsorption is irreversible. A weak adsorption of oxygen on ZnO at room temperature was reported by Putseiko and Terenin[28] and Enikeev et al.[10]; Keier[29] demonstrated the presence of "weak" adsorption at temperatures between 20° and 100°, and "strong" adsorption above 100°. The different forms of chemisorption of oxygen on zinc oxide were investigated also by Barry and Stone[30,31], who concluded that the predominant chemisorbed species at room temperature is O^- whereas above 300° the predominant form is O^{2-}, "stabilised by the diffusion of interstitial zinc towards the surface". The chemisorption of both unsaturated (ethylene, propene) and saturated (propane) hydrocarbons on metal oxides was investigated by Margolis[32]. A definite fraction of the adsorbed hydrocarbon (not more than 10%) is strongly bound to the surface, and can be removed only by baking in oxygen.

The ratio between the weak and the strong form of chemisorption is affected not only by temperature but also by the nature of the adsorbed gas and of the adsorbent. Thus, according to Keier and Kutseva[33] the amount of strongly bound CO_2 on nickel oxide (NiO) is no more than 2.5–3% of a monolayer, whereas oxygen and acetylene are strongly adsorbed, and can only be desorbed from the surface in negligibly small amounts.

Not surprisingly, the difference between the two forms of chemisorption springs from differences in heat of adsorption. Garner and coworkers showed[34] that the fraction of CO and H_2 which is reversibly adsorbed at room temperature varies from oxide to oxide. Thus, CO adsorption on ZnO at room temperature is completely reversible. The heats of adsorption vary between 12 and 20 kcal mole^{-1}. On other oxides, such as Mn_2O_3 and $Mn_2O_3.Cr_2O_3$, the heats of adsorption are higher and the chemisorption is irreversible.

Margolis showed[32] that, by introducing various amounts of impurity into the adsorbent, both the adsorption capacity and the ratio between the strong and the weak form of chemisorption can be controlled. Thus, in the adsorption of propene on magnesium chromite ($MgO.Cr_2O_3$) the proportion of the strong form is as follows: 3% in the absence of additives, 10% in the presence of 1% of added Na_2SiO_3, 25% in the presence of 2% Na_2SiO_3, and 50% of the total adsorption in the presence of 3% Na_2SiO_3.

It should be noted that any reference to two forms of chemisorption underlines the existence of different types of bond between the chemisorbed species and the surface. A more detailed study of these forms may reveal the presence of yet more types of bond.

3. Change in Electrical Conductivity and Work Function of the Adsorbent During Adsorption

The strong and the weak form of chemisorption differ in their effect on the electrical conductivity σ of the adsorbent. According to Morrison[35] and Kubokawa and Toyama[36], the weak adsorption of H_2 on ZnO, which takes place below 100°, has no effect on the electrical conductivity, whereas the strong, high-temperature adsorption increases the conductivity. The temperature beyond which adsorption begins to have an effect on σ depends on the method of preparation of the adsorbent. The activation energy for high-temperature adsorption is about twice as large as the activation energy for low-temperature adsorption. The effects on σ of the weak and the strong hydrogen chemisorption on nickel oxide are qualitatively similar to the above[37,38].

Keier's results[29] on the adsorption of ethanol on ZnO are very interesting: adsorption proceeds almost instantaneously at room temperature, and a coverage of 80–85% of a monolayer is obtained in 15–45 s. The conductivity of the adsorbent (pressed discs of ZnO) does not change during adsorption up to a complete monolayer; only after 20 min, when adsorption has gone to completion, does σ begin to increase. The increase then continues for a very long time. At 100° the adsorption of ethanol produces changes in σ two orders of magnitude higher than at 20°. The greater part of the adsorbed alcohol can be removed from the surface by heating at 450°: under these conditions ~ 50% of a monolayer is desorbed unchanged, whilst the remainder undergoes changes and emerges from the surface as CO_2 (and in part as ethylene).

The variation of the work function φ with surface coverage has been examined by Enikeev and others[10-13]. It was found that the sign of the surface charge is determined essentially by the nature of the adsorbed molecule. Changes in work function (for different gases on different semiconductors) span a fairly wide range of values: from tens of millielectron-volts to 0.7–0.9 eV. In some cases these changes are reversible, in others they are irreversible and slow to develop. The adsorption capacity, and also the dependence of φ on coverage, are related to the type of chemisorption: as a rule, the extent of adsorption of a gas is lower for exhaustive (or depletive) chemisorption than for enrichment (or cumulative) chemisorption. In the former case coverages seldom exceed 1–10% of a monolayer, and φ varies linearly with coverage. In the latter case the ultimate coverage can approach a monolayer (O_2 on NiO, C_3H_7OH on ZnO), but φ varies logarithmically with coverage.

It should be noted that a change in φ as a result of adsorption does not necessarily prove that the adsorption is chemical in character. Physical adsorption of dipolar molecules with a large enough dipole can also produce a sizeable change in φ. Such appears to be the case[10] in the adsorption of isopropyl alcohol (C_3H_7OH) on zinc oxide at 20°.

If the dipole moment of the adsorbed molecules is small, the change in φ is a measure of the bending of the energy bands at the surface of the semiconductor, and therefore also of the potential difference between the surface and the bulk. In some cases it has been shown[11] that the change in work function ($\Delta\varphi$) is equal to the change in activation energy for chemisorption (ΔE).

Simultaneous observations of the adsorption kinetics and of the kinetics of the resulting changes in the electronic properties of the semiconductor adsorbent are particularly interesting. Unfortunately, very few investigations of this type have been reported. The kinetics of changes in σ following oxygen adsorption on thin layers of oxides have been examined in a series of papers by Gray, Garner, and their coworkers[37,39], but the experiments did not include simultaneous adsorption measurements. The extent of adsorption was inferred by an indirect method: by assuming that the conductivity was proportional to the square root of the coverage.

Litovchenko and coworkers[40] arrived at the following conclusion from their study of time-changes in φ accompanying the adsorption of oxygen on germanium: "immediately after adsorption the work function φ does not change, i.e. the adsorbed molecules attach themselves to the surface in an effectively neutral state, and gradually undergo charge transfer, which in turn modifies the bending of the bands at the surface".

Enikeev has made a detailed study of the kinetics of changes in φ in conjunction with the kinetics of oxygen chemisorption on manganese dioxide[12,41]. He identifies three stages in the take-up of oxygen: the first stage consists in almost instantaneous adsorption, proceeding without activation energy. Surface coverages are very low (up to 10^{11} cm^{-2}), and the work function increases sharply by 0.20–0.25 eV. The second, and relatively slow, stage is described by the logarithmic Roginskii–Zel'dovich isotherm, Eqn. (1), both as regards coverage and work function. The latter increases linearly with the coverage, which can reach $3-6 \times 10^{12}$ cm^{-2}. Above 100° a new mechanism involving absorption of oxygen by the lattice can be observed. This gives rise to the third and slowest stage. The increase in work function during this stage is minimal.

To conclude this section on experimental studies of the kinetics of chemisorption, we must point out that, in spite of the large number of published papers (see, for example, the review article by Low[2]), very few of these have dealt with simultaneous observations of the rate of gas absorption and of kinetics of changes in the electronic characteristics of the adsorbent (such as the electron work function or the electrical conductivity). Yet, only by combining simple adsorption measurements with electronic measurements can we hope to characterise unambiguously chemisorption phenomena.

II. REVIEW OF THEORETICAL WORK

1. Difference in Approach Between the Boundary Layer Theory and the Electronic Theory of Chemisorption

The origin of the electronic theory of chemisorption on semiconductors goes back to 1947 (F. F. Vol'kenshtein). The results obtained by Vol'kenshtein and his coworkers have been published as a monograph[42]. In 1952 the electronic aspects of chemisorption on semiconductors began to attract attention in many countries: Hauffe and coworkers in West Germany, Weisz in the USA, Germain in France, etc. This work is known under the name of boundary layer theory (Randschichttheorie der Adsorption). It should be noted that until recently the kinetics of chemisorption have been practically ignored in the context of the electronic theory, most of the work being confined to equilibrium aspects of the adsorption problem.

Before proceeding to a discussion of specific contributions to the boundary layer theory (in so far as they relate to the kinetics of chemisorption), we shall dwell upon some characteristic features of the approach of the boundary layer theory to chemisorption problems in general and to the kinetic aspects in particular[8,18,43–48].

Firstly, according to the boundary layer theory a localised surface level within the forbidden gap of the semiconductor (corresponding) to a chemisorbed species) exists only in so far as it is occupied (by an electron in the case of an acceptor level or by a hole in the case of a donor level). In other words, transition to the chemically adsorbed state does not give rise to a level which, as commonly understood, can be either occupied or empty: the resulting level is by definition occupied. The localised surface levels used in the boundary layer theory to represent chemisorbed species cannot be unoccupied. Hence, during adsorption the rate of appearance of chemisorbed species can be identified with the rate of capture of electrons (or holes) by the surface levels rather than with the rate of appearance of these levels: as many chemisorbed particles appear in unit time as there are levels which can become occupied during the same time. Similarly, during desorption the rate of disappearance of chemisorbed species from the surface is identified with the rate at which electrons (or holes) can be set free from the corresponding levels.

In contrast, we note that in the electronic theory[42] the chemisorption of a species generates a localised surface level in the forbidden gap of the semiconductor which can be either free or occupied. In the former case the chemisorbed particle is in the state termed a "weak" bond; in the latter case, when a free electron (or hole) of the semiconductor becomes localised in the level, the bond between the species and the lattice of the adsorbent is stronger and the chemisorbed species is in the state termed a "strong" bond. The relative numbers of the two states (or of the two types of bond) are determined, for a given position of the surface chemisorption level, by the position of the Fermi level at the surface. The chemisorption level will be occupied by an electron (or hole) with practically unit probability only if it is located sufficiently far below or above the surface Fermi level (depending on whether we are dealing with an acceptor level or a donor level). In this case the treatment is formally the same as that of the boundary layer theory (for problems of adsorption equilibrium).

Secondly, most of the work on the boundary layer theory assumes that physical adsorption is invariably involved as a first stage necessarily preceding chemisorption. The physically adsorbed state undergoes a transition to a state in which the species is chemisorbed. The idea of physical adsorption in the boundary layer theory effectively takes the place of the idea of a "weak" form of chemisorption on which the electronic theory relies. We should also note that, as Vol'kenshtein[42] points out on p. 19 of his monograph, the electronic state leading to physical adsorption cannot produce chemical adsorption, and vice versa, so

that transition from physical to chemical adsorption necessarily involves transition of the system to a different electronic state.

One of Hauffe's papers[44] discusses a scheme in which chemisorption (of acceptor species) occurs in the absence of a physical adsorption stage: species are chemisorbed from the gas phase on to surface traps ready to receive an electron and produced by some mechanism other than adsorption. These traps are represented by some localised level in the forbidden gap. Unoccupied traps of this type take part in the act of chemisorption with the status of reactants: their concentration appears as one of the factors in the expression for the rate of adsorption. The act of chemisorption itself is, so to speak, trimolecular: it involves an unoccupied surface trap, a gas species, and an electron from the adsorbent, which is captured from the valence band if the adsorption takes place on a p-type semiconductor or from the conduction band in the case of adsorption on an n-type semiconductor. The nature of the traps is left vague: "they can have various physicochemical origins: for example, they can be physically adsorbed species". We would make the following comment on the statement that physically adsorbed species can generate localised levels in the forbidden gap of a semiconductor. It is well known[42] that the effect of physically adsorbed species on the energy spectrum of the electrons in the adsorbent is confined to a small perturbation. Hence, if such species generate localised levels they must be fairly shallow ones[49].

Hauffe's statement appears to be logical, because it ignores the "weak" bond: this is characteristic of all papers on the boundary layer theory. In fact, if the "weak" bond is effectively absent, we have two alternatives Either we operate with adsorption levels which exist only in so far as they are occupied by electrons (for the case of acceptor species), which "makes nonsense of the very concept of a localised level as a level free to accept or emit electrons",[42] or else we ascribe to physically adsorbed species the property of always generating localised levels whose occupancy is treated as a transition to the state of chemical adsorption, which can hardly be correct.

In view of the different approaches of the boundary layer and of the electronic theory of chemisorption, and also because recent papers within the scope of the electronic theory and dealing with kinetics are not mentioned in Vol'kenshtein's book[42], we shall discuss these papers separately in Section III of the present review.

2. The Boundary Layer Theory

The chemisorption of an acceptor gas was treated by Hauffe as follows[44]. (We shall use, however, the terminology adopted in the electronic theory)[42].

(a) Chemisorption on a p-type semiconductor is a reaction involving a species A from the gas phase and a surface trap B not occupied by an electron. The species A, on becoming adsorbed in the empty trap, "emits a hole into the valence band" (in Hauffe's words):

$$A+BL \rightarrow ABeL+pL,$$

where L denotes the lattice, and eL and pL are an electron and a hole in the lattice respectively. The reverse reaction gives rise to desorption. The energy relationships are summarised in Fig. 1, where B is the trapping level, AB the level of the adsorbed species, FF the Fermi level,

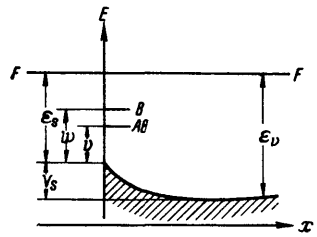


Fig. 1.

and w and v are the distances from the edge of the valence band to the trap level and to the level of the adsorbed species respectively. The overall rate of chemisorption is expressed in the form

$$dN_A/dt = k_1 P N_B (1-\eta_B)\alpha - K_2 N_A p_s.$$

Here N_A is the surface concentration of chemisorbed A species, P the pressure of adsorbed gas, N_B the surface concentration of traps, $(1 - \eta_B)$ the probability of the trap being empty, α the probability of thermal emission of a hole from the species A into the valence band, and p_S the concentration of holes just below the surface.

The following expressions are inserted for $1 - \eta_B$, p_s, and α:

$$\begin{cases} 1-\eta_B = \left(1+\exp\left[\frac{\varepsilon_s - w}{kT}\right]\right)^{-1} & (4a) \\ p_s = C_p \exp\left(-\frac{\varepsilon_s}{kT}\right), & (4b) \\ \alpha = \alpha_0 \exp\left(-\frac{v}{kT}\right), & (4c) \end{cases}$$

whence

$$\frac{dN_A}{dt} = k_1\alpha_0 \exp\left(-\frac{v}{kT}\right)\cdot\left[1+\exp\left(\frac{\varepsilon_s - w}{kT}\right)\right]^{-1}\cdot N_B P - k_2 C_p \exp\left(-\frac{\varepsilon_s}{kT}\right)\cdot N_A. \quad (5)$$

By letting dN_A/dt vanish, it is possible to determine the amount adsorbed at equilibrium; the kinetic equation (5) itself cannot be solved. At the beginning of chemisorption, when the rate of desorption is small, we can ignore the second term on the right-hand side of Eqn. (5).

If

$$\exp\left(\frac{\varepsilon_s - w}{kT}\right) \gg 1,$$

i.e. $1 - \eta_B \ll 1$, or in other words if the surface traps which play the part of adsorption centres are almost fully occupied by electrons, we obtain the following expression for the initial rate of adsorption:

$$\frac{dN_A}{dt} = k_1\alpha_0 N_B P \exp\left[-\frac{\varepsilon_s - (w-v)}{kT}\right].$$

It is not easy to see why chemisorption should require a collision between an impinging particle (species) and an

empty trap with simultaneous capture of a valence band electron by the trap, and why a collision between a particle from the gas phase and a trap already occupied by an electron (i.e. a trap in which an electron had previously become localised) should not be accompanied by chemisorption.

(b) Chemisorption on an n-type semiconductor is treated as a reaction between an empty surface trap BL, a species from the gas phase A, and a free electron from the conduction band eL:

$$A + BL + eL \rightarrow ABeL.$$

Desorption is described by the reverse reaction. The energy relationships are shown in Fig. 2, where w and v now denote the distances from the bottom of the conduction band to the trap level and to the level of the adsorbed species respectively. The equation for the net rate of chemisorption is given in the form

$$\frac{dN_A}{dt} = k_1 P N_B (1 - \eta_B) n_s - k_2 N_A \beta,$$

where

$$1 - \eta_B = \left[1 + \exp\left(\frac{w - \varepsilon_s}{kT}\right)\right]^{-1}, \quad (6a)$$

$$n_s = C_n \exp\left(-\frac{\varepsilon_s}{kT}\right). \quad (6b)$$

$$\beta = \beta_0 \exp\left(-\frac{v - w}{kT}\right). \quad (6c)$$

Here n_S is the concentration of free electrons just below the surface. Hauffe also assumes that

$$k_1 = k_0 \exp\frac{w}{kT}. \quad (6d)$$

The discussion then follows the same lines as for the case of chemisorption on a p-type semiconductor.

We should note that formula (6d) is equivalent to assuming that the rate of filling of the surface traps by electrons from the conduction band increases exponentially with their depth below the conduction band, a hypothesis which is in no way substantiated. Expression (6c), on the other hand, stated that, when a chemisorbed species is desorbed, the electron which was captured by this species is released to an adsorption centre (trap) and not to the conduction band.

Again, it is not clear why a three-body collision should be a prerequisite of chemisorption (impinging gas particle + + empty trap + free lattice electron), and why chemisorption cannot occur at a trap already filled by an electron.

In the discussion of the chemisorption of CO and H_2 on NiO (a p-type semiconductor), the first stage is assumed to be physical adsorption[45]:

$$CO + L \rightarrow CO \cdot L, \quad (7a)$$

where CO·L denotes a physically adsorbed molecule of CO.

The second stage is the transition from the physically adsorbed to the chemisorbed state:

$$CO \cdot L + pL \rightarrow COpL, \quad (7b)$$

where pL is a hole and COpL is a chemisorbed, positively charged CO molecule.

The rate of the first stage (7a) is given as

$$\frac{dN^0_{CO}}{dt} = k_1 P_{CO} - k_1' N^0_{CO} - k_2 N^0_{CO} p_s + k_2' N^+_{CO} \gamma.$$

Here N^0_{CO} and N^+_{CO} denote the surface concentrations of physically and chemically adsorbed CO molecules respectively, P_{CO} is the partial pressure of CO, and p_S the concentration of holes in the layer just below the surface.

The rate of the second stage (7b) is expressed in the form

$$\frac{dN^0_{CO}}{dt} = k_2 N^0_{CO} p_s - k_2' N^+_{CO} \gamma, \quad (8)$$

where (see Fig. 3)

$$p_s = C_p \exp\left(-\frac{\varepsilon_s}{kT}\right),$$

$$\gamma = \gamma_0 \exp\left(-\frac{v}{kT}\right).$$

Assuming that equilibrium between the physically adsorbed molecules and the gas phase is maintained at all times, Eqn. (8) takes the form

$$\frac{dN^+_{CO}}{dt} = k_3 P_{CO} \exp\left(-\frac{\varepsilon_s}{kT}\right) - k_3' N^+_{CO} \exp\left(-\frac{v}{kT}\right). \quad (9)$$

Eqn. (9) cannot be solved. From the condition $dN^+_{CO}/dt = 0$, we find the concentration of chemisorbed CO molecules corresponding to adsorption equilibrium.

Thus, Hauffe's work has been aimed at obtaining adsorption isotherms from the kinetic equations which were formulated, and not at solving these equations in order to characterise the kinetics of chemisorption. We must also point out that according to Hauffe the adsorption level undergoes charge transfer with the conduction band only in the

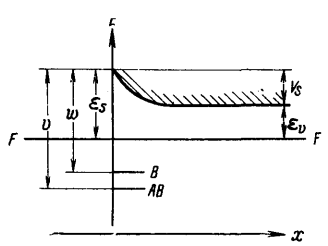


Fig. 2.

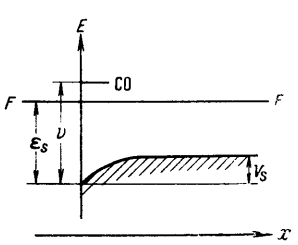


Fig. 3.

case of an n-type semiconductor and with the valence band only in the case of a p-type semiconductor. This implies that the adsorption level must be located near the conduction band for an n-type semiconductor and near the valence band for a p-type semiconductor. This hypothesis is groundless, since the position of the adsorption level in the energy spectrum depends on the nature of the chemisorbed species and on the nature of the lattice, but certainly not on the conductivity type of the semiconductor.

3. Kinetic Model of Chemisorption

Germain has discussed[18,46] what he calls a kinetic model of chemisorption. A molecule held on the surface by van der Waals forces is assumed[18] to give rise to a localised level A in the forbidden gap of the semiconductor (see Fig. 4). For concreteness, the level is assumed to be of the acceptor type. Partly ionised donors are present on the surface (level D):

$$DL \rightleftarrows DpL + eL. \qquad (10a)$$

An electron, donated by the surface donor to the conduction band, is captured from this band by the adsorption level A. As a result, the physically adsorbed A molecule is converted into an A^- ion and passes into the chemisorbed state:

$$A \cdot L + eL \rightarrow AeL. \qquad (10b)$$

Thus, chemisorption results from the consecutive transitions (10a) and (10b), and can be visualised as

$$DL + A \cdot L \rightarrow DpL + AeL. \qquad (10c)$$

It is assumed that the rate of chemisorption is equal to the rate of ionisation of the surface donors D, whose activation energy is taken to be equal to $\varphi - \chi$. The rate of adsorption is expressed in the form

$$\frac{dN_A^-}{dt} = k_1 P_A \exp\left(-\frac{\varphi - \chi}{kT}\right), \qquad (11)$$

where P_A is the pressure of the gas being adsorbed and N_A^- the surface concentration of chemisorbed species (i.e. of A^- ions), with $\varphi = \varphi(N_A^-)$. The rate of desorption is equated to the rate of the reverse reaction (10b), and is written in the form

$$-\frac{dN_A^-}{dt} = k_2 N_A^- \exp\left(-\frac{v - \chi}{kT}\right).$$

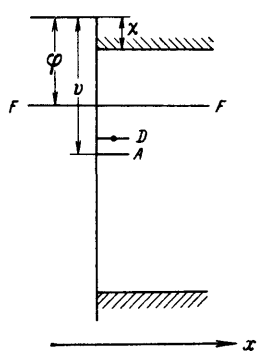


Fig. 4.

(It is evident from Fig. 4 that the difference $v - \chi$ is equal to the depth of the adsorption level below the conduction band.)

The condition of equal rates of adsorption and desorption defines the adsorption isotherm in an implicit form. At the beginning of the chemisorption process the rate is given by Eqn. (11). For small values of N_A^-, it is assumed that

$$\varphi = \varphi_0 + a(N_A^-)^2,$$

so that, taking (12) into account, Eqn. (11) becomes

$$\frac{dN_A^-}{dt} = C \exp[-a(N_A^-)^2],$$

where C and a are constants ($C > 0$, $a > 0$).

However, if a positively ionised surface donor D^+ appears on the surface for every newly produced, negative, chemisorbed A^- ion [see Eqn. (10c)], the surface charge (and therefore also the value of φ) should stay constant during chemisorption, which is of course not the case.

In Germain's[46] work the rate of adsorption is not related to the rate of ionisation of a surface impurity, but is assumed proportional to the pressure (which is taken to be constant) and, for chemisorption of the acceptor type, to the concentration n_S of free electrons in the plane of the adsorbent surface. Here $n_S \propto \exp(V_S/kT)$, so that

$$\frac{dN_A^-}{dt} = \lambda \exp\left(-\frac{V_s}{kT}\right). \qquad (12)$$

The author points out that if V_S is linearly related to N_A^- Eqn. (12) reverts to the Roginskii–Zel'dovich kinetic equation (1a), but if

$$V_s = V_s^0 - kT \ln[1 - (N_A^-)/(N_A^-)_{max}] \qquad (13)$$

the kinetic isotherm of Langmuir is obtained:

$$N_A^- = (N_A^-)_{max}[1 - \exp(-\alpha t)].$$

A similar expression for the rate of chemisorption is given by Weisz[47]: the rate of adsorption (of an acceptor gas) is proportional to the flux density of free electrons directed from the bulk towards the surface of the semiconductor, i.e. to the product of their surface concentration, their mobility, and the potential gradient at the surface.

Lastly, we shall discuss the work of Jantsch[48]. According to his model, a species landing on the surface from the gas phase is physically adsorbed and wanders on the surface until it is enabled to undergo charge transfer with the adsorbent at some surface defect. It is then converted into an ion, and this brings about the transition from the physically adsorbed to the chemisorbed state.

Furthermore, direct desorption of a chemisorbed species is considered to be very unlikely, such species disappearing from the surface only through transition to the physically adsorbed state. The kinetics of chemisorption are given by the equation

$$dN/dt = g - f. \qquad (14)$$

Here N is the surface concentration of chemisorbed species, g the increment of N per unit time resulting from transitions from the physically to the chemically adsorbed state, and f the decrement of N caused by the reverse process.

The expression for f is written in the form

$$f = N/\tau, \qquad (15a)$$

where τ is the average lifetime of a species in the chemisorbed state, and the expression for g is of the form

$$g = (\sigma z + N/\tau)w, \qquad (15b)$$

where z is the number of collisions of gas molecules with 1 cm² of the surface per second and w the probability of finding an adsorbed species in the chemisorbed state. The quantities τ, z, σ, and w are constant. We should note that the factor $(\sigma z + N/\tau)$ in Eqn. (15b) obviously expresses the increase in the concentration of physically adsorbed species per unit time. Expressing g in the form of Eqn. (15b) is equivalent to assuming that the rates of physical and chemical adsorption are in the ratio of $1:w$. This hypothesis (whose justification is not clear) excludes the concentration of physically adsorbed species from (15b).

By inserting into Eqn. (14) the expressions (15a) and (15b) and integrating we can arrive at the Langmuir kinetic isotherm:

$$N(t) = \alpha[1 - \exp(-\beta t)],$$

where

$$\alpha = \sigma z \tau w/(1-w); \qquad \beta = (1-w)/\tau.$$

Thus, all the (theoretical) papers on the kinetics of chemisorption at semiconductor surfaces considered here have the following characteristic feature in common: they treat chemical adsorption as a charged form of adsorption. The possibility of a chemical bond between an electrically neutral gas molecule and the adsorbent lattice is completely ignored. This neglect of the neutral form of chemisorption is characteristic of the boundary layer theory, and can be taken to be its most serious defect.

It can be shown[42] that desorption of species directly from the charged state is much less probable than desorption of neutral species, and therefore exchange between the chemisorbate and the gas phase occurs almost entirely via the neutral form of chemisorption. On the other hand, the transition of a chemisorbed species from the neutral to the charged state can be the rate-limiting step in a number of reactions occurring at a semiconductor surface. Garrett[50] used this approach in his theoretical study of the rate of a reaction involving the mechanism

$$\mathrm{AeL} + \mathrm{DpL} \rightarrow \mathrm{ADL},$$

where A is an acceptor species and D is a donor species.

We should note, however, that in many of the papers discussed above physical adsorption is identified with the neutral form of chemisorption to a greater or lesser extent. This is specially true of the work of Germain[18], in which the function of the neutral form of chemisorption is wholly ascribed to a state which Germain terms physical adsorption.

III. THE ELECTRONIC THEORY OF CHEMISORPTION

1. Role of the Electronic Factor in the Kinetics of Chemisorption on a Homogeneous Surface

In the last three subsections of this article we shall discuss the role of the electronic factor in the kinetics of chemisorption on semiconductors from the standpoint of the electronic theory. We shall assume that chemisorbed species can exist at the surface either in an electrically neutral or in a charged state (corresponding to the "weak" and the "strong" surface bond respectively), and that transitions between the two states are possible. To make the discussion more concrete, we shall confine ourselves to the adsorption of acceptor species.

Let us examine the kinetics of chemisorption on a uniform surface[51], at constant temperature T and pressure P. Let N^0 and N^- be the surface concentrations of chemisorbed species in the neutral and in the charged states respectively. Assuming that only the species present on the surface in the neutral state can be desorbed, whereas the charged species do not undergo exchange in any way with the gas phase, we can write

$$\left.\begin{aligned} dN^0/dt &= (a_1 - a_2) - [(b_1 + b_4) - (b_2 + b_3)] \\ dN^-/dt &= (b_1 + b_4) - (b_2 + b_3) \end{aligned}\right\} \qquad (16)$$

where

$$\left.\begin{aligned} a_1 &= \alpha_1 P(N^* - N) & a_2 &= \alpha_2 N^0 \exp(-q^0/kT), \\ b_1 &= \beta_1 n_s N^0, & b_2 &= \beta_2 N^- \exp(-v/kT), \\ b_3 &= \beta_3 p_s N^-, & b_4 &= \beta_4 N^0 \exp[-(u-v)kT], \end{aligned}\right\} \qquad (17)$$

and

$$\alpha_1 = \varkappa/N^* \sqrt{2\pi MkT}, \quad \varkappa = \varkappa_0 \exp(-E_0/kT). \qquad (18)$$

Here a_1 and a_2 are the numbers of species adsorbed and desorbed per second from 1 cm² of the surface, b_1, b_2, b_3, and b_4 are the numbers of corresponding electronic transitions per cm² of the surface per second (see Fig. 5); N^* is the surface concentration of adsorption centres, i.e. the maximum number of species which can be adsorbed on 1 cm², q^0 is the energy required to detach a neutral species from the surface (the energy of the "weak" bond), M the mass of the adsorbed species, $\varkappa$ the capture probability of a species by the surface, E_0 the activation energy attending the formation of a "weak" bond, and n_S and p_S are the concentrations of free electrons and holes in the plane of the adsorbing surface (at $x = 0$); the significance of the quantities v and u is clear from Fig. 5.

We shall also use the symbols

$$\left.\begin{aligned} 1/\tau &= \alpha_2 \exp(-q^0/kT), \\ 1/\tau^0 &= \beta_1 n_s + \beta_4 \exp[-(u-v)/kT], \\ 1/\tau^- &= \beta_3 p_s + \beta_2 \exp(-v/kT), \end{aligned}\right\} \qquad (19)$$

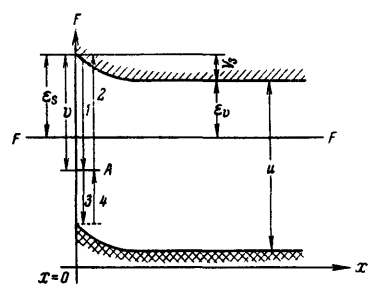


Fig. 5.

Note that $1/\tau$ defines the probability (per unit time) of desorption of a species; $1/\tau^0$ and $1/\tau^-$ are the probabilities of charging and discharging a chemisorbed species respectively. In other words, τ is the mean lifetime of a species in the adsorbed state, τ^0 and τ^- are the mean lifetimes of a chemisorbed species in the neutral and charged states respectively.

At low coverages, when

$$N \ll N^*, \tag{20}$$

the system of equations (16) can be written, using Eqns. (17)–(20), in the form

$$\left.\begin{aligned} \frac{dN^0}{dt} &= \frac{N^0_\infty - N^0}{\tau} - \left(\frac{N^0}{\tau^0} - \frac{N^-}{\tau^-}\right), \\ \frac{dN^-}{dt} &= \frac{N^0}{\tau^0} - \frac{N^-}{\tau^-}, \end{aligned}\right\} \tag{21}$$

where $N^0_\infty = N^0(\infty)$. We have made use of the fact that at $t = \infty$ we have $a_1 = a_2$, whence $\alpha_1 PN^* = N^0_\infty/\tau$.

Assuming that electronic quasi-equilibrium exists in the bulk of the semiconductor (i.e. that the distribution of free electrons and holes is approximately the equilibrium distribution corresponding to the instantaneous value of the surface charge), and that the electron and hole gases are non-degenerate, we can use equilibrium Boltzmann expressions for n_s and p_s. Under these conditions τ^0 and τ^- turn out to be functions of N^-.

If we solve the simultaneous equations (21) for constant τ^0 and τ^-, i.e. ignoring changes in the bending of the bands during chemisorption, we can analyse the kinetics of adsorption and desorption, and then proceed to show that the main features of the kinetics thus obtained do not alter appreciably when allowance is made for changes in the bending of the bands.

If electronic equilibrium exists at the surface at any given instant, t, the relative extents of the neutral and of the charged forms of chemisorption at that instant can be calculated by the well-known formulae of Fermi statistics:

$$\left.\begin{aligned} \eta^-(t) &= \frac{N^-(t)}{N(t)} = \left[1 + \exp\frac{\varepsilon_s(t) - v}{kT}\right]^{-1}, \\ \eta^0(t) &= \frac{N^0(t)}{N(t)} = \left[1 + \exp\frac{v - \varepsilon_s(t)}{kT}\right]^{-1}, \end{aligned}\right\} \tag{22}$$

where ϵ_S is the depth below the bottom of the conduction band of the Fermi level at the surface (see Fig. 5).

According to the relative values of the characteristic times τ, τ^0, and τ^-, electronic equilibrium can be preserved or destroyed during adsorption and desorption. The former regime (adsorption or desorption in which electronic equilibrium is maintained) is observed when

$$\tau^0, \tau^- \ll \tau. \tag{23a}$$

In this case (case a) the establishment of electronic equilibrium is fast in comparison with the establishment of adsorption equilibrium. Electronic equilibrium at the surface is set up long before adsorption equilibrium, and is maintained at all times. The second regime (case b) exists when adsorption or desorption causes a perturbation of the electronic equilibrium, i.e. when

$$\tau \ll \tau^0, \tau^-. \tag{23b}$$

In this case adsorption occurs in two distinguishable stages: first, equilibrium between the neutral form and the gas phase is rapidly set up, and then, in a second stage, the charged form appears whilst the concentration of neutral species remains stationary.

Either of these two limiting cases can occur in practice, depending on the nature of the adsorbent and of the adsorbate.

On the assumption that τ^0, τ^- = const, the kinetics of chemisorption after a short initial period take the form of the Langmuir equation. If allowance is made for the change in the bending of the bands during chemisorption, the kinetic isotherms usually depart from the Langmuir form. As long as electronic equilibrium is maintained, the departures from Langmuir kinetics appear only in the region close to adsorption equilibrium, whereas in the absence of electronic equilibrium these departures manifest themselves long before adsorption equilibrium is reached. Combining the two equations (21), we obtain

$$\frac{dN}{dt} = \frac{N^0_\infty - N^0}{\tau}, \tag{24}$$

whence it is evident that, as long as $N^0 \ll N^0_\infty$, the function $N(t)$ increases approximately as $N^0_\infty t/\tau$, as required by Langmuir kinetics, in the region far from adsorption equilibrium. In the case of electronic equilibrium the conditions $N^0 \simeq N^0_\infty$ necessarily implies that we are approaching adsorption equilibrium. When electronic equilibrium is disturbed, however, N^0 becomes comparable with N^0_∞ long before adsorption equilibrium is established.

The dependence of the activation energy for adsorption upon electronic parameters such as ϵ_v, V_S, and ϵ_S is quite different for the two cases a and b. If condition (23a) applies, then in the region far from adsorption equilibrium the activation energy is in general independent of the electronic parameters. This is evident from Eqn. (24), since when $N^0 \ll N^0_\infty$ we have

$$\frac{dN}{dt} = \frac{N^0_\infty}{\tau} = \alpha_1 PN^* = k\exp\left(-\frac{E_0}{kT}\right).$$

This situation obtains even if the charged form of chemisorption predominates in the adsorbate, so that the rate of adsorption is practically the same as the rate of generation of the charged form. This is not surprising if we remember that the rate of appearance of charged species (acceptors) is proportional not only to n_S but also to the concentration of unoccupied levels, i.e. the extent of the neutral form of chemisorption. It turns out that, if electronic equilibrium is maintained during adsorption and the chemisorbate is predominantly in the charged form, then the larger n_S the lower is the concentration of unoccupied levels at any instant: the net result is that the rate of appearance of charged species (and hence the rate of adsorption) becomes independent of n_S, i.e. of the position of the Fermi level.

The situation is quite different when electronic equilibrium is disturbed [case (23b)]. In the second stage, when the neutral species have reached equilibrium with the gas phase and the charged form of chemisorbate is being produced, the activation energy for adsorption includes the term ϵ_S. Under these conditions we are far from adsorption equilibrium. The rate of adsorption is given by the expression

$$dN/dt = k_0 \exp(-\varepsilon_s/kT).$$

It can be shown that this formula remains valid even when changes in band bending during adsorption are allowed for. By inserting various alternative forms of the function $\epsilon_S = \epsilon_S(N)$, we obtain various kinetic isotherms not of a non-Langmuir form. The following relationships have been observed experimentally[13]:

$$\varepsilon_s = AN + B \text{ and } \varepsilon_s = A' \ln N + B'.$$

The form of the function $\epsilon_S = \epsilon_S(N)$ has been studied theoretically by Kuznetsov[52].

2. Partial Irreversibility of Chemisorption on Semiconductors

It is well known that desorption at the temperature of the adsorption experiment does not always remove the whole of the chemisorbate from the surface. This phenomenon is termed partial irreversibility of chemisorption. We shall consider here two possible mechanisms[53,54].

The first mechanism stems directly from the model of desorption proposed for the case where electronic equilibrium is disturbed. Thus, in case *b* [see condition (23b)] the desorption of charged species lags very considerably behind the desorption of neutral species: after a time of the order of τ practically all the neutral species have left the surface, whereas the desorption of charged species is protracted over a much longer time interval, of the order of τ^-. An important consideration here is that τ^- can be very large: values of the order of 10^4–10^5 s have been computed. In this case the duration of a practical desorption experiment can be small compared with τ^-, i.e. with the time needed to remove the charged species, and hence also with the time needed for complete desorption of the chemisorbate. In these circumstances we shall be able to observe, in practice, only the desorption of the neutral form, and the charged form will appear to be almost irreversibly bound to the surface. We should note that if we abandon the assumption that only a small fraction of the adsorption centres is occupied [see Eqn. (20)], then the time for complete adsorption is found to be much less than the time for complete desorption.

The second mechanism consists in the reaction between the chemisorbate and an impurity present in the bulk of the semiconductor. For example, in the chemisorption of oxygen on ZnO the ionised interstitial zinc Zn_i^+ arriving at the surface from the bulk can react as follows with a charged, chemisorbed oxygen atom O_a^-:

$$Zn_i^+ + O_a^- \rightarrow Zn^{2+}O^{2-}.$$

This process is equivalent to an irreversible addition to the crystal lattice resulting from oxidation of the zinc in excess of stoichiometry. Many authors[30,35,45,55] have discussed the role of processes of bulk impurity extraction in chemisorption.

The most characteristic difference between the two mechanisms is that the irreversibility associated with the first is only "apparent": if desorption is allowed to proceed for a long enough time the charged form of chemisorbate ion will also be removed from the surface. On the other hand, the irreversibility associated with lattice addition can be regarded as "true" irreversibility. Furthermore, "apparent" irreversibility effects can be expected only at not too high temperatures, since τ^- falls off rapidly with increase of temperature. On the other hand, the "true" irreversibility mechanism requires a high enough mobility of the reacting impurity, and should therefore be undetectable at low temperatures, its contribution increasing sharply with increase of temperature.

Many experimental observations can be accounted for by either of these two mechanisms (for example, the large extent and large irreversibility of the adsorption of oxygen on ZnO specimens with a high content of interstitial zinc, which does not affect, however, the initial rate of desorption[30]). Therefore, it is interesting to distinguish experimentally between these two mechanisms of irreversible adsorption and to identify the mechanism which is operative under some particular experimental conditions. We shall now consider the appropriate criteria, making the following assumptions: the reaction is so slow that the equilibrium (Boltzmann) distribution of the reacting impurity in the bulk of the solid is not disturbed; chemisorption (or, more precisely, the appearance of charged species on the surface) is fast in comparison with the diffusion of the reacting impurity towards the surface; the amount of impurity removed is small in comparison with the total amount of reacting impurity in the crystal.

Based on these assumptions, the following criteria for distinguishing experimentally between "true" and "apparent" irreversibility have been obtained.

1. Let N_r and N_i stand for the reversible and the irreversible contributions to the chemisorption respectively. "Apparent" and "true" irreversibility lead to different relationships, other conditions being equal, between the ratio N_i/N_r and the bending of the bands at the surface (V_S).

In the case of "apparent" irreversibility

$$N_i/N_r \propto \exp(-V_s/kT),$$

whereas if the irreversibility is "true" and the charged form of chemisorption predominates, the expression becomes

$$N_i/N_r \propto \exp(+V_s/kT),$$

or, if the neutral form predominates in the case of "true" irreversibility,

$$N_i/N_r = \text{const.}$$

2. The kinetics of the change in the electron work function (φ) and in electrical conductivity (σ) of the adsorbent are different in the two cases. In the case of "apparent" irreversibility we should find partial irreversibility of φ (since the neutral species are desorbed, the charged species remain on the surface, and both contribute to the change in φ) and complete irreversibility of σ (since σ is determined only by the concentration of charged species, which remain on the surface, see curves *2* of Fig. 6). However, if the chemisorption is "truly" irreversible, we should observe complete reversibility of both these quantities (curve *1* of Fig. 6). In this case, both neutral and charged species are removed from the surface, since the absorption of charged species by an impurity is equivalent to their removal from the surface as regards their effect on φ and σ. Thus, direct adsorption measurements are necessary in order to identify true irreversibility.

Of course, the above statements are correct only if the surface reaction does not influence too strongly the spectrum of surface states due to causes other than adsorption.

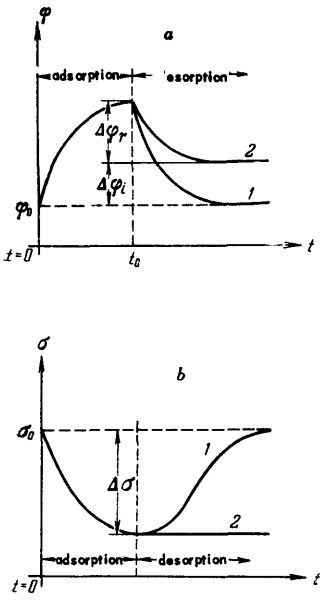


Fig. 6.

We should also remember the assumption that the impurity is effectively inexhaustible, so that ϵ_v remains constant.

An "apparent" irreversibility mechanism is evidently involved in the adsorption of oxygen on TiO_2 at room temperature: this is shown by the changes in φ and σ during desorption recently reported by Figurovskaya[56]. A "true" irreversibility mechanism can be observed at temperatures as low as 350° on zinc oxide, as reported by Glemza and Kokes[57], who made a combined study at this temperature of the adsorption of oxygen on ZnO and of the kinetics of changes in σ.

3. Electronic Aspects of the Inhomogeneity of the Adsorbent Surface

The idea of inhomogeneity in the adsorbent surface arose from attempts to explain the large fund of experimental data which do not fit into the simple model of adsorption phenomena developed by Langmuir. The theory of adsorption and catalysis at inhomogeneous surfaces, due mainly to Roginskii's school[58,59], assumes that different portions of the surface differ in their adsorption properties: their adsorption parameters (such as the heat of adsorption and the activation energy) are not the same everywhere, but each element of area shows simple (Langmuir) behaviour. Surface inhomogeneity is characterised by a definite distribution function of the elements of area with respect to activation energy and heat of adsorption.

It should be noted that the universality of the initial Langmuir model is lost[60] when allowance is made for the electronic processes taking place at the surface during chemisorption. In the electronic theory of chemisorption the adsorption and kinetic laws are not, generally speaking, of the Langmuir type, even for a uniform surface and in the total absence of direct interaction between chemisorbed species. This is because in the treatment of the adsorbent–adsorbate system as a unified quantum-mechanical system the species are "made aware" of each other through the electron gas of the adsorbent. Thus, the concept of inhomogeneity is only an additional cause for departure from the Langmuir laws.

We shall attempt here to deal with the case where the initial adsorption behaviour of the homogeneous elements of surface is non-Langmuir. In other words, the contribution of chemisorption to the surface charge is assumed small, and therefore the variation of ϵ_S with N is ignored. Only in this case can the inhomogeneity of the adsorbent surface be characterised by a distribution function specific to the surface itself: in the more general case the "distribution function" is a characteristic of the combined adsorbent–adsorbate system[60]. This approximation is equivalent to separating the effects of surface inhomogeneity and surface charging during chemisorption[61,62].

The basic problem facing the theory of adsorption and catalysis at inhomogeneous surfaces is to clarify the physical significance of the distribution function by which the theory operates. The question is: why do the different elements of surface show different activation energies or heats of adsorption? According to the ideas of the electronic theory, the adsorption properties of any part of the surface are determined by the electronic state of the system, i.e. by the position of the Fermi level in that particular element of area. Therefore, any mechanism causing the position of the Fermi level (relative to the energy bands) to vary from point to point on the surface can serve as a physical basis for surface inhomogeneity. In particular, inhomogeneity can result from uneven distribution of impurities in the bulk and at the surface of a semiconductor (even when we are dealing with impurities of a single kind). In practice, the topography of the Fermi level at the surface, i.e. its position with respect to the energy bands, is uniquely determined (as a function of position along the surface) by the distribution of impurities in the semiconductor. We must stress that the impurity in question can be one not directly involved in chemisorption (i.e. not playing a direct part in the act of chemisorption). For example, it may be an impurity located in the bulk phase. The concept of an impurity uniformly distributed in a semiconductor, widely adopted in theoretical papers, is of course greatly idealised. The inhomogeneity of the electronic properties f a semiconductor surface is a well-known fact[63–65].

As an illustration of what has been said, we shall consider the adsorption isotherm, which for a uniform surface is of the form

$$N/N^* = \theta = [1 + (b_0/P)\exp(-q/kT)]^{-1}, \qquad (25)$$

where, according to Vol'kenshtein[42],

$$q = q^0 - kT\ln\eta^0(\varepsilon_s).$$

Obviously, surface inhomogeneity implies that different areas will have different values of q. It is with respect to this quantity that averaging is carried out in the theory of adsorption at inhomogeneous surfaces. All the distribution functions which are compared with experimental adsorption isotherms in the theory are, in fact, distribution functions with respect to q. As long as we remain within the boundaries of Langmuir's molecular-kinetic model, i.e. as long as we ignore the electronic processes attending chemisorption, we have $\eta^0 = 1$, and therefore the quantity $q = q^0$ has the significance of a bond energy between the

chemisorbed species and the surface. Under these conditions the isotherm (25) is indistinguishable from the familiar Langmuir isotherm

$$N/N^* = \theta = (1 + b/P)^{-1},$$

where

$$b = b_0 \exp(-q^0/kT),$$

and any inhomogeneity results from local differences in the energy q^0 between the chemisorbed species and the surface, and can therefore be characterised by a distribution function with respect to q^0.

In the electronic theory of chemisorption differences in bond energy q^0 are not excluded, but they do not play the major role. Local differences in the position of the Fermi level ϵ_S are also possible. This will give rise to differences in the value of q for different elements of the surface, even if the bond energy q^0 is the same everywhere. In this case the surface inhomogeneity will be characterised by a distribution function with respect to ϵ_S.

In order to apply to an inhomogeneous surface a kinetic isotherm obtained for a uniform surface, some sort of averaging over a parameter of the equation is necessary. It can be shown that local differences in the part of the activation energy E_0 which does not depend on electronic parameters (i.e. differences in the capture probability of a species by the surface) do not cause departures from the Langmuir form of the kinetic isotherm (at low coverages). Non-Langmuir isotherms can be obtained in two ways, either by assuming local differences in the position of the Fermi level or by assuming local differences in the energy needed to remove a neutral species from the surface. Differences in ϵ_S may or may not lead to non-Langmuir kinetic isotherms, depending on the relative values of the time--constants τ, τ^0, and τ^-, and also on the position of the local chemisorption level with respect to the surface Fermi level. An important consideration is that if adsorption (of acceptor species) occurs under conditions such that electronic equilibrium is not maintained, and only the conduction band takes part in electron transfer processes at the surface, non-Langmuir kinetics can arise after some initial time interval only from differences in surface charge, i.e. from the fact that the kinetic isotherm was not of the Langmuir form even for a homogeneous surface. If the kinetic isotherm in this case is of the Langmuir type, i.e. of the form

$$N = A[1 - \exp(-kt)],$$

the coefficient k depends only on the position of the level associated with the chemisorbed species relative to the energy bands, and hence no averaging process can alter N.

It is clear that the role of the electronic factor in the kinetics of chemisorption on semiconductors is radically different according to whether electronic equilibrium is or is not maintained; the most characteristic kinetic features, established experimentally, are indeed those which refer to the case of disturbed electronic equilibrium. These include: (1) the non-Langmuir character of the kinetic isotherms, whose shape is determined, as shown by the work of Enikeev, Margolis, Roginskii, Rufov, and others, by the form of the function $\epsilon_S = \epsilon_S(N)$, i.e. by the way in which the work function varies with coverage; (2) the dependence upon electronic parameters of the activation energy for adsorption. Thus, the assumption that electronic equilibrium is maintained during chemisorption is far from always being justified, and is not a theoretical necessity.

Further progress in the study of kinetics, and therefore also of chemisorption on semiconductors, must await new investigations, particularly experimental ones, of the kinetics of chemisorption (in the usual meaning of the word) coupled with a study of the accompanying changes in the electronic state of the adsorbent and of the species held on its surface.

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ELECTRONIC PROPERTIES AND STRUCTURE OF POLYMERIC ORGANIC SEMICONDUCTORS

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I. INTRODUCTION

Polymers with conjugated bonds occupy a central place in an interesting new class of compounds, that of organic semiconductors, which includes also low-molecular-weight one-component compounds with conjugated bonds (for example, condensed aromatic systems, dyes, etc.), individual charge-transfer complexes, some biological materials such as proteins, and charcoals. The intensive research devoted to these polymers, which were first synthesised as recently as the late 1950's,[1-4] has aroused wide interest in the problem and has created a borderline science: the physics and chemistry of organic semiconductors†. The main attraction of polymers in this context is the fact that their chemical configuration and their structure can be modified as required, thus providing an unlimited number of materials on which to study the nature of the specific properties of organic semiconductors and the modification of these properties in a desired direction.

In recent years, many reviews and monographs have been written on the methods of preparation[24-27] and on the properties[13-17,21,28-37] of semiconducting polymers. It is now recognised that polymers with conjugated bonds, like organic semiconductors of other classes, have a specific type of electronic and atomic structure which gives rise to a combination of properties uncommon in organic compounds: a special electrical and magnetic behaviour, high thermal stability, low solubility, reactivity of a specific kind (in particular, catalytic activity‡), etc. In the present review, which includes all work published up to January

† Progress in the study of organic semiconductors of various classes has been discussed in a number of books and reviews[5-23].

‡ Papers on the catalytic properties of semiconducting polymers, already fairly numerous, will not be considered here because of lack of space. See, for example, Refs. 38–43 and also p.778.