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EXPERIMENT AND THE ELECTRONIC THEORY OF CATALYSIS†

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1. INTRODUCTION

In the present lecture I shall endeavour to discuss the electronic theory of catalysis from the point of view of the experimentalist who wishes to apply its results rather than from the point of view of the theoretician who is contributing to its development. I shall be talking of the experimental material on which the theory is based: that which has given rise to the theory and that which, in turn, stems from the theory.

Some simple relationships exist in general (and in the field of catalysis, in particular) between physical theory and experiment which can be expressed by the trite statement that theory divorced from experiment is effectively meaningless whilst experiments lacking a theory are blind. Experiment is the fertile soil in which theory can grow; theory, like a theatrical spotlight, throws light on experiment.

The electronic theory of catalysis has a twofold aim: on the one hand, to reveal the elementary mechanism of the catalytic act and at the same time to discover the relationship between the chemisorption and the catalytic properties of a surface, and on the other hand to relate those characteristics to the electronic properties of the crystal as a whole. The electronic theory of catalysis does not, in general, conflict with other contemporary theories of catalysis: it differs from them only in its approach to the problem. It is concerned with the elementary (electronic) mechanism of the phenomenon, and it tackles problems in catalysis from just this point of view.

The electronic theory of catalysis proved to be the gate through which contemporary solid state theory and the theory of the chemical bond, together with their associated quantum mechanics and quantum statistics, were able to enter the field of catalysis. The history of science has no comparable examples to offer of an invasion by physics of the territory of chemistry. Consider, for instance, the theory of the chemical bond, which even 50 years ago consisted of nothing more than dashes denoting valencies. Quantum mechanics has given those dashes a physical content, thus uncovering the physical nature of chemical forces.

We can distinguish two aspects of the interplay between the electronic theory of catalysis and experiments, which the present article aims to discuss.

Firstly, the theory provides an explanation of known experimental facts. These can be *old* facts, fitting more or less well into old theories, on which the electronic theory throws new light. Or they can be *new* facts, transcending the scope of the older theories, and deriving some theoretical interpretation, for the first time, from the electronic theory.

Secondly, the electronic theory leads to a number of experimental predictions. Like any other theory, it contains explicit or implicit rules and relationships which can be (and should be) identified and tested experimentally.

It is useful and interesting to gather together and analyse the basic experimental material which is satisfactorily interpreted by means of the electronic theory and which can therefore be entered on the credit side.

At the same time, it is particularly interesting to collect and analyse all the corollaries of the electronic theory still awaiting experimental confirmation. Such is the aim of the present paper.

This paper is divided into three sections of unequal length and importance: (1) first of all we shall deal (rather briefly) with some well known experimental facts on which the electronic theory has thrown new light; (2) we shall then list (again, rather briefly) some predictions of the electronic theory which have already been confirmed; (3) lastly, and this will form the major part of the paper, we shall attempt to summarise those theoretical predictions still awaiting experimental confirmation.

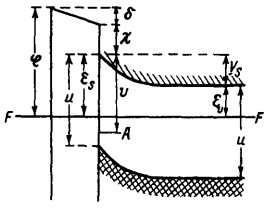


Fig. 1.

2. SOME OLD FACTS IN A NEW LIGHT

a. "Induced" Non-Uniformity

When discussing well-established experimental facts to which the electronic theory has given new meaning one should mention first of all the reluctance of real surfaces to show Langmuir adsorption behaviour.

Classical theory copes with this fact by introducing the concepts of surface non-uniformity or interaction between adsorbate particles. The electronic theory introduces yet a third alternative: a special kind of "interaction, transmitted through the electron gas, which enables each chemisorbed particle to experience the presence of all the others despite the absence of direct force interactions[1,2]. This effect arises because the properties and the nature of the bond between each individual particle and the surface are determined by the state of the whole system of adsorbent + adsorbate. We are also dealing with a special kind of "non-uniformity", because at any given time particles of a single kind form different types of bond with the surface. This is the effect to which Boudart recently applied, rather unsuccessfully, the term "induced non-uniformity".[3]

Allowing for this special kind of "interaction" or of "non-uniformity" — the two concepts are equivalent in this context — brings the Fermi level[4] into the expression for the differential heat of adsorption q. Thus, it follows from the electronic theory that[1]

$$q = q^0 - kT \ln (1 - \eta), \tag{1}$$

where q^0 is the binding energy between a chemisorbed particle in its electrically neutral state and the lattice of the adsorbent, and η is the proportion of the charged form of chemisorption on the surface. The quantity η is of the form

$$\eta = \frac{1}{1 + \exp [\pm (\varepsilon_s - \upsilon)/kT]}, \tag{2}$$

so that, substituting (2) into (1), we arrive at the following expression for q:

$$q = q^0 + kT \ln \{1 + \exp [\mp (\varepsilon_s - \upsilon)/kT]\}. \tag{3}$$

The significance of the symbols adopted here is clear from Fig. 1, showing the energy diagram for a semiconductor, on which FF denotes the Fermi level and A is the localised surface level associated with an adsorbed particle. In formulae (2) and (3) we must choose the upper or the lower sign according to whether the adsorbed particle is an acceptor or a donor. If $\eta = 0$, that is, if all the particles are in the same (electrically neutral) state, Eqn. (1) gives $q = q^0$ (the classical result).

The Fermi level ϵ_S, as well as the heat of adsorption q, enters into the isotherm equation

$$\theta = \frac{1}{1 + (b/p) \exp (-q/kT)}, \tag{4}$$

where q has the form of (3). Of course, the position of the Fermi level at the crystal surface, ϵ_S, is itself a function of the degree of coverage of the surface, θ:

$$\varepsilon_s = \varepsilon_s (\theta). \tag{5}$$

Thus, Eqn. (4) is still not an isotherm equation, because it does not explicitly contain the variation of θ with p. By solving Eqn. (4) for θ we obtain various non-Langmuir isotherms (corresponding to different approximations) which agree with experimental observations. This was done by Kogan and Sandomirskii[5] as long ago as in 1959.

In this way, the electronic theory leads to non-Langmuir isotherms for surfaces which are uniform (in the classical sense) and in the absence of interactions between adsorbed particles (again, in the classical sense).

b. Physical Nature of the "Distribution Function" in the Theory of Non-Uniform Surfaces

"Induced non-uniformity", a concept typical of the electronic theory, does not, of course, prelude surface non-uniformity of the usual type. The phenomenological theory of adsorption at a non-uniform surface developed by Roginskii's school[6] can be fitted, in its entirety, into the electronic theory. Furthermore, some of the concepts acquire a new significance thereby. We can take as an example the concept of a "distribution function", fundamental in Roginskii's theory yet lacking physical significance in that theory, which serves to characterise the non-uniformity of a surface.

Consider a surface which is "non-uniform with respect to the heat of adsorption q". This means that the surface consists of different areas characterised by different values of q. The "distribution function with respect to the heat of adsorption q" which we shall denote by $F(q)$, where q varies over some interval between q_{min} and q_{max}, gives the fraction of the surface characterised by a given value of q. By definition

$$F(q) = ds/dq, \tag{6}$$

where ds is the fraction of the surface for which q lies between q and $q + dq$.

If ϵ_S varies over the surface, the latter will have, according to Eqn. (3), a non-uniform behaviour with respect to the heat of adsorption q even if the binding energy q^0 is constant for all points on the surface. We must remember that the value of ϵ_S, that is, the depth of the Fermi level below the conduction band in the plane of the surface, is determined by the concentration of impurities at the surface and in the bulk of the crystal. Therefore ϵ_S will vary from point to point of the surface if the impurities in the crystal are not homogeneously distributed, that is, whenever a concentration gradient of impurity exists along

the surface — the impurity can be of one and only one given kind, and does not itself take part in the act of adsorption: the only requirement is that it must be distributed non-uniformly.

For each arrangement of the impurity there will be a corresponding "distribution function" $F(q)$. In this way, the "distribution function" acquires some physical meaning. The problem was recently discussed by Peshev and the present author[7]. We shall list, as an example, some of their results.

The first example concerns the distribution function

$$F(q) = ds/dq = \text{const}, \quad (7)$$

that is, a uniform distribution of the elements of surface with respect to heat of adsorption, which can be realised by a gaussian arrangement of the impurity along the surface (around any point taken as the origin):

$$N(r) = C \exp(-r^2/r_0^2), \quad (8)$$

where $r = \sqrt{x^2+y^2}$, the coordinate axes x and y lying in the plane of the surface, and N being the concentration of impurity at the surface.

Second example. An exponential distribution function

$$F(q) = ds/dq = \alpha \exp(-\beta q) \quad (9)$$

is obtained when the impurity arrangement is parabolic:

$$N(x) = C(x - x_0), \quad (10)$$

where β and γ are uniquely related.

Thus, the various non-uniform arrangements of the impurity give rise to various "distribution functions". This is a possible interpretation of the "distribution function", but not the only possible one.

c. Active Centres

Another concept very widely used in the study of catalysis, and physically even less understood than the "distribution function" in the theory of adsorption at non-uniform surfaces, is the concept of "active centres". The term refers to specific points on the surface which support the catalytic reaction, in contrast to the remainder of the surface, which is catalytically inert.

The notion of "active centres", without specifying their physical meaning, is all that is required to construct a phenomenological theory of catalysis. This leaves obscure, however, the physical nature of such active centres. In Kobozev's theory of ensembles the active centres are identified with various combinations of catalyst atoms (pairs, groups of three, etc.), the catalyst being deposited as an amorphous phase on a catalytically inert substrate. A. A. Balandin's multiplet theory dispenses with this concept altogether. However, as a rule the concept of "active centres", devoid of any concrete physical significance, is widely adopted by students of catalysis.

According to the electronic theory[1], the catalytic activity of a surface is determined by the fraction of the total number of chemisorbed molecules which is found to be in a reactive state. The reactive molecules are those in the form of radicals or radical-ions, unlike the valency-saturated molecules, which are considered to be unreactive to a first approximation. As in other theories of catalysis, "active centres" are invoked: a molecule is in a reactive state when it is adsorbed at an "active centre". It is the binding to the "active centre" which makes the molecule reactive.

In the electronic theory, free (unsaturated) surface bonds play the role of "active" centres. These include valencies freely wandering along the surface, pointing from the surface into the bulk of the crystal, and pointing from the bulk towards the surface. Alternatively, the free valencies can be fixed (localised) at various structural defects of the surface. It can be shown that free electrons and holes in the crystal lattice play the role of unsaturated valencies. Thus, these entities fulfil the function of "active centres" in the electronic theory.

Having adopted this model for the "active centres", we should be able to predict some of their properties. Generally speaking, the centres are not immobile: they wander along the surface until they encounter chemisorbed molecules to which they become bound. This causes localisation of the centres. At the same time, the binding of the molecule to the surface becomes stronger, and the molecule is converted into a radical-ion and becomes reactive. Alternatively, the "active centre", having spent some time bound to the molecule, can break free and resume its wandering along the surface. When this happens the molecule left on the surface loses its reactivity and reverts from the radical-ion to the valency-saturated (and therefore electrically neutral) state. The concentration of "active centres" of this type on the surface is not fixed: they can be supplied from the bulk of the semiconductor (or, conversely, they can be adsorbed into the bulk) both during catalyst preparation and in the course of the reaction.

Thus, the idea of "active centres" acquires a concrete physical meaning in the electronic theory, and this clarifies their properties and their mode of operation.

d. Reversible and Irreversible Form of Chemisorption

As a further example of the way in which old facts acquire a new meaning in the light of the theory we shall consider the problem of the reversible and the irreversible form of chemisorption: the coexistence of both these forms appears to be characteristic of semiconductors.

From the point of view of the electronic theory, particles chemisorbed at a semiconductor surface can be either in an electrically charged or in an electrically neutral state. Under conditions of electronic equilibrium the relative amount of each kind is strictly fixed. However, electronic equilibrium can be disturbed in a number of instances. It is never achieved in the early stages of adsorption, and it can be destroyed during desorption. This type has been examined in detail in a recent paper by Peshev and the writer[8].

In this system, only the neutral form of chemisorbate, effectively, leaves the surface. Only later, as they become discharged, do the particles in the charged state vacate the surface. In this way, slow electronic transitions can inhibit the desorption process. If desorption of the charged form is sufficiently slow, it can be treated as irreversible. A significant increase of temperature is needed to remove the adsorbate completely from the surface.

Thus, the neutral and the charged form of chemisorption can, under certain conditions, behave as the reversible and the irreversible form respectively. This also

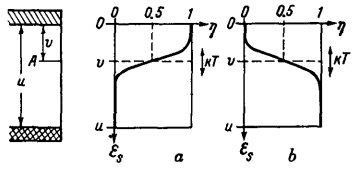


Fig. 2.

explains the occurrence of the two forms of chemisorption: it is one possible (but not the only possible) mechanism for the appearance of the two forms of chemisorption so familiar to the experimenters.

To conclude this section, we shall note that the coexistence of neutral and charged chemisorption forms on the surface is one of the crucial conclusions of the electronic theory. We must always remember, however, and this remark applies particularly to experimentalists attempting to "confirm" or "refute" the electronic theory, that under a given set of conditions practically the whole of the particles chemisorbed on the surface will be found in the neutral state (or alternatively in the charged state). Instances in which both forms are present in comparable amounts are quite rare.

This should be clear from Fig. 2, which shows, on the basis of Fermi statistics, the variation of the fractional amount of the charged form, η, with the position of the Fermi level, ϵ_s, under conditions of electronic equilibrium for acceptor particles (Fig. 2*a*) and for donor particles (Fig. 2*b*). A is the localised level due to the chemisorbed particles. We can see that the quantity η differs appreciably from zero or from unity only when the Fermi level lies fairly close to the level A (within a distance smaller than or of the same order as kT).

Thus, it is possible to convert the neutral (reversible) form of chemisorption into the charged (irreversible) form or vice versa by shifting the Fermi level, that is, by varying the conditions or the previous history of the sample.

3. SOME PREDICTIONS WHICH HAVE BEEN CONFIRMED

a. Relationship between Catalytic Activity and Electrical Conductivity

Turning now to the predictions of the electronic theory which have already been put to experimental test, we must, of course, point out first of all the relationship between the catalytic activity and the electrical conductivity of a semiconductor. The correlation between these two characteristics was predicted theoretically[9] as early as in 1950, when no experimental work of any kind existed in this field.

At the present time we can refer to a whole series of researches in which this correlation has been experimentally observed: many workers have measured the electrical conductivity and the catalytic activity of differently treated samples, and have observed a direct or an inverse relation between these two characteristics of the semiconductor on going from sample to sample.

We shall not enumerate all these investigations: they are quite well known. We shall only refer to a few of them to illustrate the point. Keier and coworkers[10] studied the oxidation of carbon monoxide on specimens of nickel oxide containing different amounts of lithium added as an impurity. They established an unmistakable inverse relationship between activity and electrical conductivity: the higher the initial conductivity, the lower was the activity of the material. Rienäcker[11] studied the decomposition of dinitrogen monoxide on the same semiconductor, nickel oxide, doped with different amounts of aluminium. He found that the electrical conductivity and the activity varied in the same sense. The same result was obtained by Heckelsberg and coworkers[12] in their study of the hydrogen–deuterium exchange reaction on zinc oxide containing various impurities.

b. Relationship between Catalytic Activity and Work Function

The thermionic work function is another parameter which physically characterises a semiconductor and which, according to the electronic theory, should be related to the catalytic activity even more directly than the electrical conductivity.

The electrical conductivity is determined by the value of ϵ_v (the depth of the Fermi level below the conduction band in the bulk of the crystal, see Fig. 1), whereas the adsorption properties and the catalytic activity are determined by the quantity ϵ_s (the depth of the Fermi level at the surface). There is a definite relationship between ϵ_v and ϵ_s, but this can often be distorted or obscured, thus upsetting the correlation between electrical conductivity and activity. On the other hand, the work function φ (see Fig. 1), ignoring the dipole contribution δ and to the accuracy of the constant term χ, is equal to ϵ_s by definition ($\varphi = \epsilon_s + \chi + \delta$). It is therefore unequivocally related to the adsorption properties and to the catalytic activity.

A correlation between catalytic activity and work function, that is, a variation in the same or in the opposite sense between these two quantities, was predicted in theoretical papers[2] published in 1948–1950. Many papers published since that date have described experimental confirmations of this theoretical prediction: we shall not attempt to list them comprehensively here. Two examples will suffice. Margolis and coworkers[13], in their study of the oxidation of propene on copper(II) oxide doped with various impurities, observed an inverse relationship between activity and work function: the materials with the lowest work function were the most active in causing complete oxidation. A similar correlation was found by Zhabrova and coworkers[14], who investigated the dehydrogenation of isopropyl alcohol on variously doped specimens of zinc oxide.

c. Changes in Work Function and Electrical Conductivity upon Adsorption

When discussing the relationship between the work function and the electrical conductivity of a semiconductor on the one hand, and between the work function and the adsorption properties and catalytic activity on the other hand, we often have in mind the changes in work function and electrical conductivity induced by adsorption itself, or occurring in the course of a catalytic reaction, rather than just a correlation between these two quantities among a number of differently prepared samples. The effect is caused by

the charging of the surface upon adsorption, leading to a shift of the Fermi level and a change in the concentrations of free electrons and holes in the layer of semiconductor immediately below the surface.

The charging of adsorbed particles resulting from the localisation of free electrons or holes from the crystal lattice onto those particles, was demonstrated theoretically as long ago as in 1948–1951 [2,9,15]. The effect has now been studied experimentally in fair detail on a variety of systems. Experimentalists often use it to establish the nature (acceptor, or donor) of the adsorbate when the nature of the adsorbent is known (n- or p-type semiconductor). It can also be used to establish the nature of the adsorbent if the nature of the adsorbate is known.

We shall not attempt to review all these experimental investigations. They are very numerous, and quite well known. Indeed, we must beg the indulgence of the readers for dwelling on familiar material in this section of the paper.

d. The Photoadsorption Effect

The photoadsorption effect must be mentioned among those instances in which theory did not follow experiment, but rather led the way. The effect can be positive or negative: an increase or a decrease in the adsorption properties of the material under the influence of light. It was discovered, and originally investigated, by Terenin and coworkers, and by Hedwall, in the 1930's. However, the factors which determine the sign of the effect remained obscure for many years.

The first attempts [4] to set up a theory of the photoadsorption effect, in 1958, showed that the sign of the effect depends, under otherwise constant conditions, on the previous history of the specimen, and can be changed by suitable pretreatment. Shortly afterwards, Fujita and Kwan [16], working in Japan, were able to demonstrate sign inversion for oxygen on zinc oxide by controlling the departure from stoichiometry of the sample.

Further theoretical work by the writer and Karpenko [17] showed that the sign of the effect is determined by the position of the Fermi level within the crystal, ϵ_v, and by the bending of the bands, V_s (see Fig. 1). Fig. 3, reproduced from that paper [17], shows the region of possible values of ϵ_v and V_s compatible with a Boltzmann distribution of free carriers throughout the crytal for acceptor particles on an n-type semiconductor (for example O_2 on ZnO). The straight line AA divides this region into areas of positive and negative effects, denoted by different cross-hatching on the Figure. The segment v (compare Fig. 1) indicates the position in the energy spectrum of the crystal of the localised surface level corresponding to the adsorbate particles of the kind being considered; the segment V_s characterises the initial bending of the bands, existing in the absence of any adsorbed particles on the surface and therefore caused by surface states arising otherwise than by adsorption; u denotes the width of the forbidden gap between the bands. It is evident that we can pass from the region of positive to the region of negative photoadsorption effect, and vice versa, by shifting the Fermi level ϵ_v, or by changing the band bending V_s, or by changing both parameters at the same time.

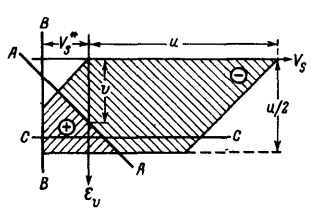


Fig. 3.

In the light of this theoretical prediction, it is relevant to mention some recent results obtained by Kwan [18], who studied the effect by investigating the adsorption of oxygen on zinc oxide containing lithium or aluminium. In the former a positive effect was observed, in the latter a negative, as was indeed to be expected on the basis of Fig. 3, since the replacement of an acceptor impurity (lithium) by a donor (aluminium) must always move the Fermi level upwards. Referring to Fig. 3, we see that this may cause a transition from the region of positive photoadsorption to the region of negative photoadsorption.

Also in agreement with Fig. 3 are some recent results of Haber and Kowalska [19], who investigated the same system (oxygen on zinc oxide). Oxidation of the surface was found to change the effect from positive to negative, as required by Fig. 3. This is because oxidation of the surface is accompanied by an increase in V_s, which causes a shift from left to right in Fig. 3 (for example, from the positive effect towards the negative effect region).

e. The Electroadsorption Effect

We shall consider one other phenomenon predicted theoretically in 1958 and experimentally observed only very recently. This is the phenomenon for which we have suggested the term "electroadsorption effect".

The theory leads us to expect a change in the adsorption properties of a semiconductor upon application of an external electric field normal to the adsorbent surface. This effect, resulting from the displacement of the Fermi level under the influence of the field, was computed by Sandomirskii and the writer [20] for a semiconductor located between two condenser plates and therefore retaining electrical neutrality when the field is applied. For the field effect technique, when the semiconductor under study acts as one of the electrodes and acquires an induced charge upon application of the field, the calculation was carried out by the writer in cooperation with Baru [21].

The field effect method, though widely used in semiconductor studies and ideally suited to the investigation of the role of electronic factors in chemisorption and catalysis, is only just beginning to make its first tentative steps in catalysis laboratories, owing to a number of specific practical difficulties. Thus, the use of single crystals (which is the rule in field effect experiments) makes it difficult if not altogether impossible to carry out direct adsorption measurements. The extent of adsorption has to be inferred indirectly from the change in surface conductivity. The electrical charge in the gas phase, which appears at not too low pressures and high enough fields, is another complication. Great care is needed to ensure that the new effect being sought is not confused with trivial electrochemical effects.

Among the experimental studied we can single out that of Lyashenko and coworkers[22], and also that of Mikheeva and Keier[23], who actually observed the expected change in the adsorption properties of the surface under the influence of an external electrical field (adsorption of acceptor and of donor gases on germanium). The former used a direct adsorption method (by monitoring pressure changes in the adsorption volume), the latter relied on changes in electrical conductivity.

4. SOME PREDICTIONS STILL AWAITING CONFIRMATION

We have now reached the final, yet the most important, section of the paper. We shall examine a numer of predictions implicit in the electronic theory which have not yet been fully formulated, or subjected to experimental test.

a. Role of an External Electric Field

We must deal first of all with the phenomena stemming from the influence of an external electric field on the properties of the surface.

The field effect method, already considered above, can be used as a new and very sensitive procedure for determining the surface coverage of the charged form of chemisorption, and can also be used to measure adsorption on single crystals. The electric circuit for the field effect method is shown in Fig. 4*a*: the current i is measured as a function of the field strength E. The specimen is shown cross-hatched in Fig. 4*a*.

Fig. 4*b* shows some typical field effect curves (variation of the surface conductance σ with E). The heavy line corresponds to a specimen in a vacuum: the thin line corresponds to the same specimen in a gaseous medium (the diagram refers to conditions when the adsorbent is an n-type semiconductor and the adsorbate behaves as an acceptor). Assume that we are at point A on the heavy curve; admission of gas takes us to point B, showing a fall in conductance from the initial value σ_0 to σ_1. We now change the field by an amount ΔE (from E_0 to $E_1 = E_0 + \Delta E$), in such a way as to travel along the thin curve from point B to point C. This restores the conductance to its initial value σ_0.

From the value of ΔE we can arrive at the amount of charge gained by the surface as a result of adsorption. We have

$$\Delta E = -(4\pi e/\varkappa) N^-, \qquad (11)$$

where N^- is the surface concentration of chemisorbed particles which are in the uncharged state, e is the absolute value of the electronic charge, $\varkappa$ is the dielectric constant of the gaseous medium.

Thus, from the "compensating" field ΔE and from the dependence of ΔE on E_0 we can determine both the surface coverage by the charged form, N^-, and the "electroadsorption effect", that is, the change in the above coverage brought about by the external field (N^- as a function of E_0):

$$N^- = N^-(E_0).$$

This simple "compensation method" is the most direct way of measuring the effect of an external field on the adsorption properties of the surface.

As regards the effect of the field on the catalytic activity (acceleration or inhibition of the catalytic reaction by the applied field), an effect for which we propose the name "electrocatalytic effect", it also follows from the theory and for the same reasons, but it still remains a theoretical prediction awaiting experimental confirmation. Experimental studies of the effect of an external field on the chemisorption and catalytic properties of a semiconductor surface are only just beginning. We may hope that they will expand in the coming years.

b. Role of a Magnetic Field

A magnetic field should have an effect similar to that of an electric field. Consider a plane-parallel slab of a semiconductor to which are simultaneously applied an electric and a magnetic field, parallel to the adsorbing surface but mutually perpendicular (see Fig. 5). Due to the Hall effect one of the surfaces will be depleted of current carriers whilst the other is enriched by the same factor. As a result, the adsorption capacity of the specimen as a whole becomes greater, as we shall proceed to show.

Let N_0 be the concentration of chemisorbed particles on each of the surfaces in the absence of a magnetic field, and ΔN_1 and ΔN_2 be the increments caused by the magnetic field on the two adsorbing surfaces respectively. As can readily be shown[21] we have

$$\left.\begin{aligned} \frac{\Delta N_1}{N_0} &= \eta_0\left[\exp\left(-\frac{\Delta V_s}{kT}\right) - 1\right], \\ \frac{\Delta N_2}{N_0} &= \eta_0\left[\exp\left(+\frac{\Delta V_s}{kT}\right) - 1\right], \end{aligned}\right\} \qquad (12)$$

where $-\Delta V_s$ and $+\Delta V_s$ are the changes in surface potential V_s (see Fig. 1) induced by the magnetic field on the corresponding surfaces, and η_0 is the relative amount of the charged form of chemisorption on the surface in the absence of the magnetic field.

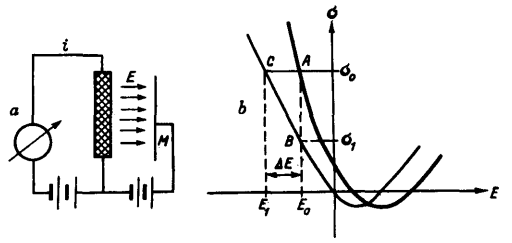


Fig. 4.

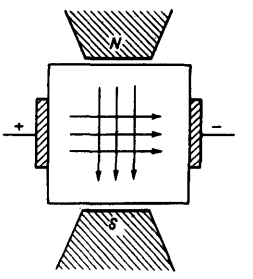


Fig. 5.

Clearly,

$$\left.\begin{array}{ll} \text{if} & \frac{\Delta N_1}{N_0}<0, \text{ then } \frac{\Delta N_2}{N_0}>0, \\ \text{if} & \frac{\Delta N_1}{N_0}>0, \text{ then } \frac{\Delta N_2}{N_0}<0. \end{array}\right\} \quad (13)$$

The relative change in the adsorption capacity of the specimen as a whole becomes, from Eqn. (12):

$$\frac{\Delta N}{N_0}=\frac{\Delta N_1}{N_0}+\frac{\Delta N_2}{N_0}=4\eta_0 \sinh^2\frac{\Delta V_s}{kT}\geqslant 0. \quad (14)$$

The increased adsorption capacity can be detected not by direct adsorption measurements, which would be very difficult under the conditions of this experiment, but from the changes in electrical conductivity occurring during adsorption. The change should be more pronounced in the presence than in the absence of a magnetic field (provided, of course, that all the other conditions remain the same).

It can be shown that the magnetic field will increase, at the same time as the adsorption capacity, also the catalytic activity towards any catalytic reaction which proceeds by an electronic mechanism.

c. Role of Illumination

Let us return to the photoadsorption effect, already discussed above. We shall define the magnitude of the effect by the quantity

$$\Phi=\frac{\Delta N}{N_0}, \quad (15)$$

where N_0 is the concentration of adsorbed particles in the dark, ΔN is the increment brought about by the illumination. The quantity Φ is the relative change in the adsorption capacity of the surface under the influence of light. Obviously, Φ can be positive (photoadsorption) or negative (photodesorption).

Fig. 6 shows the theoretical curve for the variation of the photoadsorption effect Φ with position of the Fermi level in the bulk of the crystal ϵ_v (see Fig. 1). The Figure, reproduced from a paper by the writer and Karpenko[24], refers to acceptor-like adsorbed particles. The quantity u in Fig. 6 denotes the width of the forbidden gap between the bands, V_s is the bending of the bands, v is the depth of the localised energy level A due to the chemisorbed particle below the conduction band. The meaning of the symbols used is made clear by comparing Figs. 6 and 1.

It is obvious from Fig. 6 that we must expect a correlation between the magnitude of the photoadsorption effect and the initial dark conductivity of the semiconductor, determined by ϵ_v: the greater ϵ_v, the smaller will be the electronic conduction and the greater the hole conduction in the semiconductor. We see that if all other conditions are equal the algebraic value of the photoadsorption effect should be higher, the smaller the dark conductivity of the specimen. This is true, as can also be seen from Fig. 6, of n- and p-type semiconductors alike: the former corresponds to the upper half of Fig. 6 ($\epsilon_v < u/2$), the latter to the lower half ($\epsilon_v > u/2$). It would be interesting to test this prediction experimentally. Equally interesting would be a study of the photoadsorption effect in conjunction with the field effect, that is, a study of the combined effects of light and of an external electric field on a semiconductor. This is because an external field allows the band bending V_s to be varied over very wide limits without affecting the value of ϵ_v. In other words, a change in the intensity of the external field results in a horizontal movement in Fig. 3 (for example, along the line CC), and it is evident from Fig. 3 that this may lead to a change in the sign of the photoadsorption effect. We must expect, therefore, that sometimes either photoadsorption or photodesorption will occur on a particular specimen under a constant set of conditions, according to the magnitude and direction of the external electric field applied to the specimen.

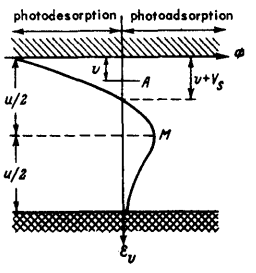


Fig. 6.

d. Role of Impurities

An electric field, a magnetic field, and illumination are factors which affect the chemisorption and catalytic properties of a semiconductor, all things considered, by the same mechanism. They bring about a change in the concentration of the electron or hole gas at the crystal surface. This is enough to explain the mechanism of their influence on the chemisorption properties and on the catalytic activity of a surface.

Impurities added to the bulk of the crystal are yet another factor involving the same mechanism. This statement applies to impurities contained in the crystal in a state of atomic subdivision; impurities forming a separate phase are, of course, excluded. Impurity effects on the activity of a catalyst (catalyst promotion or poisoning) have been known for a long time; they are now well characterised from the point of view of experiment as well as theory (including the electronic theory).

The effect of impurities on the adsorption properties of a surface has received much less attention. We refer to impurities added to the bulk of the crystal and not wholly residing on the surface. Impurities deposited on the surface can act as adsorption centres, or, conversely, they can block existing adsorption centres. We are not concerned here with this simple mechanism of impurity action, but with the influence of impurities on the properties of the surface through their effect on the electronic state of the system as a whole, not involving direct contact between the impurity and the adsorbate.

The electronic theory predicts a decrease in the adsorption capacity of the surface for acceptor gases, and an increase in the adsorption capacity for donor gases, when an acceptor impurity is added to the crystal. A donor impurity should have the opposite effect. It must be noted, however, that a given impurity will behave as an acceptor or as a donor not only according to its own nature, but also according to the nature of the crystal to which it is

added and to the way in which it is added to the host crystal. By the same token, adsorbed molecules behave as acceptors or donors according to the nature of the centres on which they are adsorbed as well as to their own nature. The unambiguous criterion of the acceptor or donor role of an impurity is the way in which it affects the electrical conductivity (whether it increases or decreases the electron and the hole contributions to the conductivity). The unambiguous criterion of the acceptor or donor role of an adsorbed molecule is its effect on the work function (whether it increases or lowers it, respectively).

If we compare the adsorption of a particular gas under otherwise constant conditions on differently doped specimens of a given semiconductor we expect to find a family of adsorption isotherms such as those shown in Fig. 7, which are numbered in order of increasing (or decreasing) concentration of impurity in the crystal.

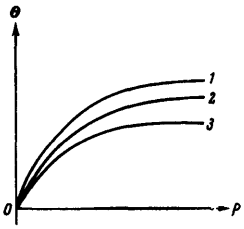


Fig. 7.

At the same time, we should expect a correlation between the adsorption capacity and the electrical conductivity, similar to the correlation which exists between catalytic activity and electrical conductivity (see Section 3, a). For an *n*-type semiconductor the adsorption capacity towards an acceptor gas should change in the same sense as the electrical conductivity and the adsorption capacity towards a donor gas should change in the opposite sense. For a *p*-type semiconductor the reverse is true.

Of course, such a correlation can be expected only if the impurity added to the bulk of the semiconductor has no effect at all on the system of surface states. The correlation between electrical conductivity and work function can be used as a criterion that such is the case.

Impurities which affect the relative amounts of the neutral and the charged form of chemisorption in the surface affect *ipso facto* the relative proportions of reversible and irreversible chemisorption. We can expect, therefore, that different amounts of irreversibly adsorbed gas will be retained, on pumping, by specimens with different impurity concentration, even if the nature of the gas and all other conditions are constant.

An experimental study of the influence of impurities dissolved in the semiconductor upon the adsorption properties of the semiconductor surface would be very interesting. Such a study, however, would meet with a number of practical difficulties. One would have to ensure that the impurity was entirely within the semiconductor, and that none had been retained on the surface, in order to observe this effect in a "pure" form.

e. Semiconducting Films on Metals. Role of Disperseness

We shall discuss the results of yet another theoretical piece of work susceptible to (but still awaiting) experimental test. The writer has investigated, with Sandomirskii and Kuznetsov[25], the adsorption and catalytic properties of a thin semiconductor film covering a metal surface. It is well known that many metals are covered, under most conditions, with a film of a binary compound, that is, they are clad with a semiconductor coating. Statements as to the catalytic action of a metal often relate, in fact, to the catalytic action of this semiconductor film. This has been stressed on many occasions by Roginskii[26] and others. If, however, the thickness of the film is small compared with the dielectric screening length of the semiconductor, then the adsorption and catalytic properties can be shown to depend on the thickness of the film and on the properties of the metal substrate: the film behaves as if it were "translucent" to the characteristics of the metal.

In most practical instances, the semiconductor film arises as a result of oxidation of the metal, and its thickness can often be controlled to some extent. The film of copper(I) oxide which grows on a copper matrix is a typical example. By varying the thickness of the coating, it is possible to apply a measure of control on the adsorption capacity, the catalytic activity, and the selectivity of the specimen. This effect is due to the fact that the position of the Fermi level in a film of this type depends on the thickness of the film. It would be interesting to study the adsorption and catalytic properties of a semiconducting film on a metal, and their changes, during growth of the film.

There is another effect which can be said to have the same origin: the variation of the specific (that is, calculated per unit surface area) adsorption capacity and catalytic activity of very finely divided materials with degree of dispersion (or grain size). This effect was studied theoretically by Kogan[27] four years ago. It offers yet another topic for experimental work, yet another incursion of theory into experiment.

f. Relationship between Differential Heat of Adsorption and Work Function

We shall return now to formula (3), which expresses the variation of the differential heat of adsorption q with the position of the Fermi level ϵ_s at the surface of the crystal, and also to Fig. 1. It can be seen from the diagram that the electron work function, labelled φ in Fig. 1, is related to the Fermi level ϵ_s, by definition, as follows:

$$\varphi = \epsilon_s + \chi + \delta, \qquad (16)$$

where δ is the so-called "dipole contribution" to the work function (that is, the additional potential step at the crystal surface arising from the polarisation of the adsorbed molecules), whilst χ is a constant which characterises the lattice of the adsorbent (the affinity of the ideal lattice for a free electron), so that the differential heat of adsorption q is unambiguously related to the work function φ if we ignore the dipole contribution δ as is commonly done.

Thus, a correlation between the differential heat of adsorption and the work function can be expected under certain conditions. As the surface coverage is progressively increased the differential heat and the work function should vary together and in the same sense if the adsorbate behaves as a donor, or in the opposite sense if it behaves

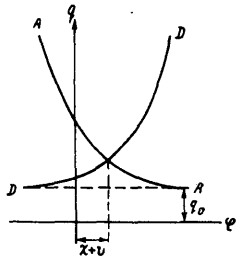


Fig. 8.

as an acceptor. The two cases correspond to the upper and lower sign in formula (3) respectively. Fig. 8 is an idealised plot of the relationship between q and φ for the adsorption of donor (curve DD) and of acceptor species (curve AA) on the assumption that $\delta = 0$.

This is yet another theoretical prediction amenable to experimental test.

We must now bring to a close this list of predictions stemming from the theory and ready to be handed over to the experimental scientists in the hope of enlisting their active interest. This is not because the list is now complete but rather because it would be unrealistic to attempt to make it complete in the space of one article.

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In conclusion, I would like to deal with a number of criticisms which could be levelled at the present article, and argue with an imaginary opponent. We can forsee three kinds of criticism (this is the last of the "theoretical predictions").

Firstly, it could be argued that the suggested experiments are difficult, and perhaps even unrealistic, for a number of reasons. To this I would reply that the present paper does not propose any definite procedures: we have only put forward the ideas of a few experiments with no other aim than to bring them to the attention of the experimental scientists. The present list of theoretical predictions, though idealised and curtailed, is a list of the points of arrest in the development of the theory where the theoretician would like to meet the experimenter.

Secondly, a list of facts which the theory has so far failed to explain could be contrasted with the facts which have been interpreted more or less successfully by the theory. There may well be unexplained facts, and more may come to light in increasing numbers. But these facts are the fertile soil in which the theory can continue to grow, improve, and perhaps even remodel itself in parts.

Thirdly, and lastly, facts allegedly in conflict with the theory could be put forward. Of course, theory must be judged by experiment. We always begin with experiment and always come back to it. However, as experiment itself shows, the experimental investigations which "refute" the electronic theory (and also, indeed, some of those which "confirm" it) should be treated with greater caution. Often these investigations, despite the claims of their authors, "refute" nothing and "prove" nothing, being the outcome of an insufficiently critical reading of the theory.

What, then, can the theoretician and the experimenter ask of each other when they meet on the domain of catalysis? The experimenter cannot, of course, expect from the electronic theory predictions of the numerical values of various physical quantities: he can expect the theory to discover the physical mechanism of the observed rules, and to predict new rules and relationships. We must therefore remember that in the field of catalysis (as indeed, in every other field) reality is immeasurably more complex than any theory and never ceases to challenge our understanding. As for the theoretician, he has the right to expect from the experimenter not casual observations but experiments which put a clear question to Nature and elicit an answer.

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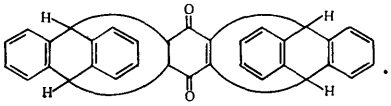
STEREOCHEMISTRY OF HYDROGENATION AND HYDROGENOLYSIS

E.I. Klabunovskii

Optically active compounds and compounds whose molecules have a rigid three-dimensional configuration may prove extremely useful in the study of the mechanism of catalysis and the structure of the active surface of catalysts. The advantages of catalytic studies of this kind arise because the initial molecules has a definite well known configuration and it is possible to construct stereochemical models for the intermediate complexes, to follow the stereochemical reaction pathways, and to obtain information about the structure of the active surface of the catalyst.

Such studies are being made both to investigate the geometry of the catalyst surface, using reactions of molecules with a complex three-dimensional structure, and to elucidate the configurational and energy interactions between the groups of the optically active compounds adsorbed on the surface.

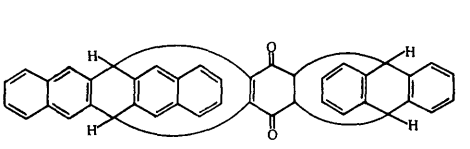
The first approach to the study of the active surface of catalysts has been achieved by hydrogenating triptycene derivatives[1] such as 2,3(9,10-anthrylene)-5,6-(9,10-anthrylene)-2-cyclohexene-1,4-dione (I), for example:



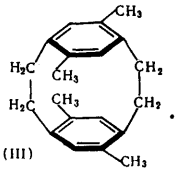
(I)

The hydrogenation of the C=C bond in the central ring of this compound occurs at an appreciable rate on a nickel catalyst even at 45°.[1] The preservation of the rigid structure of the molecule during the catalytic process, which excludes any appreciable deformation or reversal of the configuration by an S_N2 mechanism, makes it possible to construct stereochemical models of the active centre. Since chemical valence forces are of short range, the molecules are in contact with the catalyst via the reacting C=C atoms, which determines the orientation of the molecule during catalysis. The edgewise orientation on the surface is excluded in this case by the structure of the molecule and therefore it is necessary to postulate a planar disposition of the central ring on the (111) plane of the nickel crystal. Since the molecule has a complex three-dimensional structure, it cannot lie flat on this plane and it must be assumed that the correct orientation of such a molecule on the centre requires a projecting centre bounded by the (111) plane and adjacent to a number of "hollows" where the non-reacting parts of the molecules are located. On the basis of the actual dimensions of the molecular model, the height of the projecting centre in an optimum catalyst of this kind must be not less than 4.30 Å.

On catalysts with both "rougher" and more "even" surfaces the reaction of such a compound is hindered because of the reduced probability of occurrence on the surface of centres corresponding to the structure of the reacting molecule. Equally, the reaction rate may be reduced also because of an increase in "catalytic difficulties" as a result of an increase in the complexity of the three-dimensional structure of the molecule, for example when instead of compound (I) compound (II) is hydrogenated:

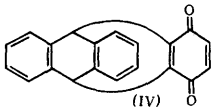


(II)

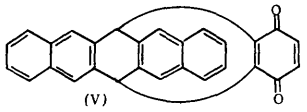


(III)

It is interesting that tetramethyl[2,2]paracyclophane (III)[2] is not hydrogenated at the usual temperature and pressure on 10% Pd/C catalysts or PtO_2. In the general case breakdown of the coplanarity of the molecule hinders hydrogenation. However, when the non-coplanar part of the molecule is not in immediate contact with the catalyst, as, for example, in the hydrogenation of triptycenequinone (IV) and dibenzotriptycenequinone (V), the rates of hydrogenation (1 atm, 45°) are almost indistinguishable[3].

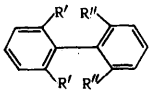


(IV)

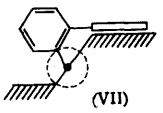


(V)

The structure of the molecule is the decisive factor in the catalytic reaction and when the structure is sufficiently complex and rigid, preventing the contact of the molecule with the active catalyst surface, the reaction cannot be achieved. For example, the biphenyl derivatives (VI)[4] are not hydrogenated as a result of the hindrance of the catalysis by the substituents R′ and R″ [structure (VII)], while hydrogenation of triptycene derivatives, although small, is in fact possible[3]:



(VI)



(VII)

The study of the catalytic reactions of homologous compounds with a complex three-dimensional configuration allows the statistical distribution of the active catalyst centres with respect to size to be found in principle[5].

Another approach which makes it possible to estimate not only the geometry of the active catalyst surface but also to take into account the energy interaction between the catalyst and various functional groups in the substrate molecule is the study of the mechanism of the hydrogenolysis of optically active compounds[6]. In this reaction the bond C*–X at the asymmetric carbon atom of the molecule (VIII) is ruptured with formation of the compound (IX); since the reaction involves the asymmetric centre, this