treated separately with equimolar quantities of diethyl phosphite. The ethyl esters of α-diethylaminomethyl- and α-diisopropylaminomethylphosphonic acids were obtained in almost quantitative yields.

Attempted Reaction of α-Hydroxymethylphosphonic Esters with Amines.—The ethyl ester of α-hydroxymethylphosphonic acid[5] was heated with diethylamine. There was no reaction at 56° after six hours or at 110° in a bomb after six hours. At 175° the mixture gave a dark resinous mass, in which the odor of phosphine was evident.

Preparation of Acetone-ethylimine.—A mixture of one mole of acetone, a 5% excess over one mole diethylamine and 10 g. of anhydrous potassium carbonate was refluxed for 30 minutes. The cooled organic layer was separated, dried over anhydrous potassium carbonate and filtered. It was not distilled, but used as such. The yield was about 80%.

Preparation of Phosphorous Acid Diesters.—Diethyl phosphite was purchased from Victor Chemical Company, Chicago, Illinois. The other phosphite esters were obtained by alcoholysis. A 10% excess over two moles of alcohol, one mole diethyl phosphite and 20% xylene based on the volume of diethyl phosphite was heated at 140° until 80–85% of the theoretical amount of ethanol had distilled. The reaction mixture was distilled *in vacuo*. The yields were about 85%. Esters of alcohols higher than 2-ethylhexanol would probably be difficult to distil without considerable decomposition.

Great care should be taken in the distillation of di-(2-chloroethyl) phosphite not to admit air until the distilling flask has cooled. At temperatures above 130° in air, decomposition occurs, phosphine is liberated and the entire mass ignites.

The phosphite esters used boiled as follows: di-*n*-amyl phosphite 107° at 1.4 mm.; di-2-ethylhexyl phosphite 145° at 1.3 mm.; di-(β-chloroethyl) phosphite 130° at 2.2 mm.

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[5] The preparation and properties of esters of α-hydroxyalkyl phosphonic acids will be described in a forthcoming publication.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Electronic Chemical Potential in Chemisorption and Catalysis

BY M. BOUDART

The electronic chemical potential of a semi-conductor changes with temperature and impurity concentration. This variation is essential to the properties of semi-conducting surfaces in adsorption and catalysis. A qualitative discussion of induced heterogeneity and of its consequences may be given on the basis of a simple model of a catalyst surface. Active centers are still essential but their localized description becomes superfluous. A consequence of the dynamic picture of a catalytic surface presented here is the necessity of devising methods for characterizing the surface during the global catalytic reaction.

The role played by the electronic chemical potential of a clean metal in chemisorption, solubility of gases and catalysis has been recently emphasized by various investigators.[1–4] Fruitful correlations between heats of chemisorption or activation energies of certain catalytic reactions and the chemical potential of the metallic electrons or the Fermi level have thus been obtained. Since the Fermi level of a metal is practically independent of temperature but may be modified by alloying elements, a study of alloy catalysis seems quite appropriate, as was early recognized by Rienäcker.[5]

On the other hand, the literature on chemisorption and catalysis describes especially the behavior of non-metallic surfaces, "dirty" or "practical" catalysts. Among these must be included the so-called metallic catalysts which have not been prepared by special techniques (*e.g.*, evaporation), in order to obtain clean surfaces. Although such surfaces are not amenable to a quantitative theoretical analysis at the present time because of our ignorance of their surface energy levels, it seems worthwhile nevertheless to examine how the variation of the electronic chemical potential in non-metallic solids may affect adsorptive and catalytic properties.

(1) The Nature of an Adsorbent Surface.—It will be assumed that a non-metallic adsorbent surface may be treated as a two-dimensional semi-conductor system. Qualitatively, the well-known results of semi-conductor theory, as applied to three-dimensional crystals, may be applied to our model of an adsorbent surface. From a quantitative point of view, the following particularities must be pointed out: (1) the distribution of energy levels at the surface is different from the one prevailing in the bulk of the crystal. (2) Departure from stoichiometry on the surface is not limited to low values, as is usual in the bulk material owing to structural limitations. Similarly, impurities may be present at the surface in concentrations substantially larger than would be tolerated by the three-dimensional lattice without phase separation. (3) Impurity levels in the two-dimensional matrix have a threefold origin (a) deviations from stoichiometry, (b) foreign admixtures introduced into the adsorbent matrix during its preparation, (c) the adsorbed species. Vol'kenshtein[6,7] has emphasized the necessity of including the impurity levels due to chemisorbed atoms or molecules. (4) The results of semi-conductor theory which will be required do not depend on the validity of the band description of ionic solids. They may be derived from straightforward thermodynamical arguments, as developed by Wagner and Schottky.[8] Applicability of Maxwell–Boltzmann statistics is all that is required. Nevertheless, for the sake of clarity, the usual band representation will be used, in conformity with general practice. For instance, Wright and Andrews[9] successfully interpret their data obtained with NiO on the basis of a

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simple semi-conductor band model although the band approximation fails in the case of NiO.[10]

(2) **Chemical Potential of the Electrons for an Adsorbent.**—It is a characteristic feature of semi-conductors that their Fermi level may be pushed upward or downward by several e.v. depending on temperature and concentration and type of impurities. The Fermi level is the energy level for which the probability of occupancy by an electron is equal to $^1/_2$: all levels a few kT's above the Fermi level are free; all levels a few kT's below the Fermi level are occupied. The energy of an electron at the Fermi level is equal to the electronic chemical potential in the system.[11] The dependence of the Fermi energy on the parameters of a semi-conductor may be summarized as follows: (1) in a simple excess semi-conductor (Fig. 1), for a constant number of donor impurities, the Fermi level E_F decreases when the temperature T increases: at $T = 0$, E_F lies mid-way between E_d and E_c; at very large T, E_F lies mid-way between E_c and E_v. At constant T, E_F moves upward with increasing concentration of donor impurities. (2) In a simple defect semi-conductor, E_F increases with T at constant acceptor concentration and decreases when the acceptor concentration increases at constant T (Fig. 2). (3) If, at constant T, an increasing concentration of acceptors is added to a simple excess semi-conductor, E_F moves downward. If conductivity is measured during this process, a curve similar to the curves characterizing conductimetric titrations[12] is obtained. Conversely, E_F moves upward when donors are introduced into a simple defect semiconductor. Conductivity curves for the latter process have been recorded[13] during the addition of CO to an oxidized copper oxide film.

(3) **Differential Adsorption Heats on a Semi-conductor.**—It is postulated, as in the case of metals, that chemisorption is accompanied by an electron transfer from the chemisorbed species to the solid adsorbent or *vice versa*. The adsorption mechanism need not be considered at this stage. As a result of the electron transfer, an ionic chemisorption bond is not necessarily formed: in fact, all intermediates between covalent and ionic bonds are possible, as is also true for the matrix itself.

TABLE I

N_D (cm.$^{-3}$)	10^{16}	10^{18}	10^{20}	10^{22}
n/N_D	0.98	0.50	0.1	0.01

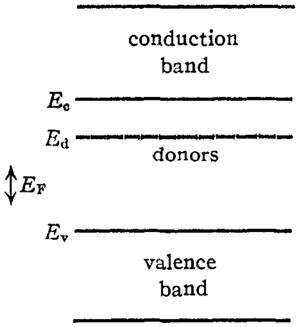

Fig. 1.—Simple excess semi-conductor.

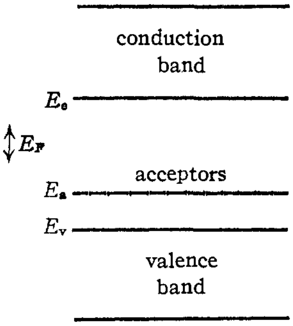

Fig. 2.—Simple defect semi-conductor.

According to the direction of electron transfer, the chemisorbed species behaves as a donor or an acceptor. If the chemisorbed species is electropositive (donor type) and if chemisorption starts on a clean surface (no impurity) and is performed isothermally, we have to deal with case (2) of the foregoing paragraph: the Fermi energy of the surface semi-conductor increases with coverage. As a result, the average ionization of the adsorbed particles decreases as their concentration increases: the ratio n/N_D of the concentration of ionized donors n to the total concentration of donors N_D, is given[14] at a constant temperature, say T = 300°K., for a value of $E_c - E_d = 0.1$ e.v. (Fig. 1) in Table I.

It must be stressed that this effect is a direct consequence of mass action and has nothing to do with "interaction" between donors. This direct interaction becomes effective only at high surface coverage. The theory derived here is valid only if interaction between impurities may be neglected, that is, in our case, for small surface coverage θ.

Now, when the Fermi energy increases and thus the ionization of the donor impurities decreases, the chemisorption heat of the donor should decrease. Consequently, differential adsorption heats of a donor impurity decrease when θ increases. By reversing the arguments, a similar conclusion is reached for the case of a chemisorbed species of the acceptor type. This well-known adsorption law is obtained here without recourse to "interaction" between adsorbed particles nor *a priori* heterogeneity of the adsorbent surface. It seems proper to follow Beeck[15] in calling this effect "induced heterogeneity." This change in the Fermi energy with adsorption seems to provide an answer to the question as to how[11] "the adsorbent surface participates in the spread of the forces between the adsorbed particles, by acting in some way as a "transmitter" of these forces." This question has been raised by Frankenburg[16] and also by Rideal and Trapnell[17] in connection with the variation of heats of chemisorption of hydrogen on tungsten. Although we confine our attention to non-metallic adsorbents, we suggest that a similar effect is responsible for "induced heterogeneity" on metals. In our case, the Fermi energy is proportional to ln N_D, so that, if $E_F \propto q$ we expect a differential heat curve of the type $q \propto \ln \theta$: such a curve would formally be interpreted by an exponential distribution of energy sites.[18] We now see how such a distribution is induced on the surface by chemisorption itself although it did not exist *a priori* and is only the formal expression of a

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fait accompli. Evidently, *a priori* heterogeneity may be pre-existing before induced heterogeneity, as suggested by the experiments of Kummer and Emmett.[19]

(4) **Model of a Catalyst Surface.**—The equilibrium composition of a working catalyst surface should depend on all internal and external parameters: (1) temperature, (2) pressure, composition and nature of the reactants and products, (3) nature of the matrix of the catalyst, (4) nature and concentration of the impurities introduced into the matrix during its preparation. This is a direct consequence of the treatment of a catalyst surface as a *unique system*, including all sorts of impurities and in particular the ones originating in reactants and products. At equilibrium, the Fermi energy of the catalyst surface will be adjusted to a level determined by the 4 parameters listed above and in accordance with the principles just outlined.

This statement, qualitative and trivial as it may seem, involves a number of theoretical and practical consequences. Fundamentally, it rests on the recognition that the catalyst surface is a *one-phase system*, as was demonstrated by Wagner and Hauffe[20] for the case of oxidation catalysis. Their arguments are based on Langmuir's interpretation of interface reactions and are perfectly general: if there are two separate phases partaking in the reaction, then reaction occurs at their boundary; the velocity of formation of a given phase will not in general be equal to the velocity with which it disappears; thus one phase will grow to the detriment of the second one, until finally one phase only is present.

The one phase catalytic system can only be fully defined with the help of the 4 groups of parameters mentioned above and such a definition looks like a rather formidable proposition. The rapidly accumulating evidence relative to the properties of defect crystals gives only a faint idea of the multitude of possibilities which may affect electron transfer at a catalyst surface, a defect phase *par excellence*.

The shift in Fermi level accompanying changes in donor and acceptor concentrations is illustrated by the following instances: (1) Pretreatment of a hydrogenation catalyst usually involves reduction in hydrogen. Oxidation catalysts are often prepared in an oxygen or air atmosphere. A catalyst pretreated in this manner will be characterized by a Fermi level quite different from the one it will possess when in contact with reacting gases. Thus an induction period with the simultaneous shift in Fermi level will normally be observed. This induction period may be beneficial or detrimental. A beneficial induction period during which activity of a reduced catalyst increases has been observed with ammonia catalysts for both synthesis and decomposition[21,22] and appears in a striking fashion in Fischer–Tropsch synthesis where it can be of a quite long duration.[23] It is commonly said that a Fischer–Tropsch catalyst has to reach its "oxidation–reduction" equilibrium. A detrimental induction period is often recorded with oxidation catalysts, *e.g.*, NiO and MnO_2 for carbon monoxide oxidation. The kinetics, during this period of strongly decreasing activity, is not expressible by any algebraic order but obeys the equation $dq/dt = a \exp(-\alpha q)$[24,25] where q is the quantity of product formed at time t. Bruns[26] has discussed this effect which he attributes to the formation of a new surface phase responsible for the steady state catalytic process. In particular, it has been shown[27] that this detrimental induction period for CO oxidation on a MnO_2 catalyst disappears either after repeated use of the catalyst with evacuation at temperature or after a pretreatment of MnO_2 with CO.

(2) The concept of a one phase defect catalytic surface with a Fermi level adjusted to the working conditions of the reaction also restricts the applicability of the isotopic method as a tool for determining the mechanism, and in particular the slowest step of a catalytic process. The data of Emmett's school on adsorption at an ammonia catalyst surface[28] are consistent with the representation of such a surface after reduction, as a phase containing Fe, Al, K and O. A working catalyst surface should also contain N and H. Arguments favoring the view that nitrogen adsorption is the slow step in the synthesis have been provided by the isotopic exchange experiments of the Princeton laboratory[29,30]: the rate of N isotopic exchange is very sensitive to the removal of a small quantity of oxygen by reduction at 500°.[31] The exchange velocity increases with the care of the preliminary reduction, but it also increases[29] in presence of hydrogen: thus both the absence of some "tenaciously held" oxygen (an acceptor) and the presence of some adsorbed hydrogen (a donor) modify the complex surface phase in the same direction. On the other hand, small amounts of oxygen or water vapor as well as incomplete reduction of the catalyst *increase* the rate of hydrogenation of chemisorbed nitrogen.[32] These results emphasize the delicate balance which is realized in a working catalyst surface and cast some doubt on the generality of conclusions reached on the basis of separate isotopic experiments performed in conditions differing substantially from the conditions prevailing during the course of the global reaction. A similar conclusion was reached by Halsey[33] who showed that the very concept of a slow step may lose its meaning on a heterogeneous surface. The

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modification of a catalyst surface by all chemisorbed species responsible for induced heterogeneity clearly restricts the applicability of the kinetic scheme of Langmuir, as amplified by Hinshelwood and Schwab. Indeed, a given adsorbate does more than "cover" a surface: by changing the Fermi energy, it also changes the ability of the surface to chemisorb other species. A good example is provided by N_2 and H_2 chemisorption[28] on a singly promoted ammonia catalyst: the surface capable of holding 37.2 cc. of chemisorbed hydrogen (a donor) at 100°, was shown to be able to hold 44.8 cc. after 14.5 cc. of nitrogen (an acceptor) had first been chemisorbed.

(3) A logical consequence of these ideas is the fact that the best catalyst for accelerating the rate of a given reaction say, from left to right, is not necessarily the best one for the reverse reaction, from right to left, in different thermodynamic conditions. This statement is of course not in conflict with Ostwald's principle which says that a catalyst should accelerate a reaction equally in both directions, since the nature of the catalyst surface changes with pressure and composition of the gas phase. Thus, addition of alkali to a singly promoted ammonia catalyst, decreases the rate of ammonia decomposition but increases the rate of the synthesis.[22] The beneficial action of alkali in the synthesis is slight at 30 atm. but becomes considerable at higher pressures (100 atm.). Storch[23] (p. 98) found that addition of chromium oxide to a zinc oxide catalyst increased its activity in the methanol synthesis but did not change its activity in the methanol decomposition.

(4) The problem of promoter action is intimately connected with the thermodynamic picture presented above: a promoter is a donor or an acceptor impurity. A systematic study of the effect of a small concentration (less than 1%) of a given impurity on rate processes at a given surface, ought to provide the necessary information for putting the principles exposed in the preceding paragraphs on a quantitative basis. One should work with low impurity concentrations in order to avoid interaction between impurities. The empirical methods of catalyst preparation, *e.g.*, by coprecipitation of two salts in almost equal proportions, prevent us from using most of the best literature data, insofar as the distribution of promoter in the matrix or the structure of the matrix itself are very often unknown.

The problem of promoter action, however, is a problem in surface rate processes and as such it cannot be solved by thermodynamic considerations alone. Besides the value of the Fermi energy and its modifications by added impurities, one has to consider the electronic configuration of the available levels. Thus, the value of the Fermi energy of copper cannot explain why the activation energy for hydrogen chemisorption on copper is equal to 20 kcal[34]: this may be understood if one attributes to empty *d* orbitals the ability to chemisorb hydrogen: *d* levels in copper are fully occupied except perhaps at higher temperatures where a *d* electron may be excited to the higher lying *s* levels, the activation energy for chemisorption originating in the solid adsorbent.[35] Vol'kenshtein[6,7] has given a theory of promoter action on the basis of a semi-conductor model: he explains the variation in the frequency factor of the rate of a catalytic reaction by considering the changes in Fermi energy with increasing concentration of impurities of a given type. He shows that on addition of increasing amounts of a donor impurity, the rate of a reaction $a\mathrm{A} + b\mathrm{B} \rightarrow$ products where A is an acceptor and B a donor should increase if $b = 0$, decrease if $a = 0$ and pass through a maximum if $a \neq 0$, $b \neq 0$. In the latter case, the same impurity first acts as a promoter but subsequently as a poison. Vol'kenshtein's theory may be applied to the recent results of Wagner[36] who showed that addition of 1% of Ga_2O_3 to ZnO increases the rate of catalytic decomposition of N_2O, as might be expected since N_2O is an acceptor and small Ga concentrations increase the concentration of donor impurities in ZnO and thus increase the Fermi energy, as witnessed by a rise in electrical conductivity. A rate measurement is however of little value without a measurement of activation energy, just as a knowledge of conductivity must be supplemented by a knowledge of activation energy for conduction.[37]

Recent conductivity data[38] show that the activation energy for conduction of ZnO does not change with addition of Al_2O_3, so that most probably, in the case of ZnO + 1% Ga_2O_3 also, the activation energy for conduction is the same as for ZnO. Thus, Wagner's observations on the rate of decomposition of N_2O may well indeed be explained by a change in the pre-exponential factor alone, following a mere increase in Fermi energy. A much larger change in the rate would have been obtained with an impurity introducing new impurity levels, thus changing the activation energy for both the reaction and the conductivity. Such is the case, for instance, when 1% CeO_2 is incorporated in ThO_2: the activation energy for H_2 oxidation drops from 24 kcal. for ThO_2 to 2 kcal. for ThO_2 + 1% CeO_2.[39] Here, the promoter action may not be explained solely with the help of the Fermi energy.

Conclusion

From the dependence of the Fermi energy of an adsorbent surface on the presence of impurities and adsorbed species, it follows that a working catalyst surface must be depicted as a defect one phase system in an "intermediate state" (Zwischenzustand) in the sense of Hüttig's school.[40] Many experiments aiming at a detailed observation of this intermediate phase, *e.g.*, adsorption measurements, isotopic exchange, perturb the catalytic surface and introduce an indeterminacy into the results obtained. A similar warning relative to this indeterminacy has recently been given by McGeer and Taylor[28] who write: "It would seem evident that studies of reactions at surfaces by indirect techniques, *i.e.*, adsorption and isotope exchange should

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be conducted with extreme caution. Unless experimental conditions in the two cases are identical, such subsidiary reactions may occur on parts of the surface which are not operative in the catalysis." Our picture of a catalyst surface which must be defined with the help of *all* effective parameters both external and internal, gives a clear understanding of this perturbation. At the same time, the induced heterogeneity of our model of a catalyst surface in an intermediate state of dynamic equilibrium gives fresh information on the nature of the active centers. The existence of active centers depends on the postulate that *all the sites* may not be active *all the time*. In the past, various efforts have been made to identify the centers with points, holes, edges, steps, planes, etc., with the idea that only a *fraction of the sites* is active *all the time*. These attempts now appear futile: the postulate may also be fulfilled if *all the sites* are active only *part of the time*. This dynamic picture of the active centers is a direct consequence of our model of a catalyst surface.

Acknowledgment.—I wish to thank Professor H. S. Taylor for many helpful discussions during the course of this work.

PRINCETON, NEW JERSEY RECEIVED SEPTEMBER 27, 1951

[CONTRIBUTION NO. 173 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Oxidation of Stannate(II) Ion by Some Cobalt(III) Complexes[1]

BY RICHARD C. PINKERTON AND FREDERICK R. DUKE

The oxidation of stannate(II) ion by hexammine- and hydroxypentamminecobalt(III) ions was found to be zero-order in the cobalt(III) concentration. Upon standing in strongly basic solution, however, the hydroxypentamminecobalt(III) was found capable of participating in a rate-determining reaction. For the hexammine complex, the reaction was found first-order in hydroxide concentration and near half-order in stannate(II) concentration. It is proposed that stannate(II) ion exists in solution chiefly as a dimer, and that some active form of the monomer is responsible for the reduction. Of a number of anions tested for catalytic effect, cyanide and thiosulfate were found to accelerate the reaction. However, the hexacyanocobaltate(III) ion cannot be reduced by stannate(II) ion. Cyanide is also the only one of the pseudohalides tried which will replace ammonia in the cobalt(III) complexes at a rate appreciable enough to influence the reduction.

Introduction

The reactions of complex cobalt(III) ions with stannate(II) ion are of interest for several reasons. First, much information can be obtained concerning the effect of certain anions on the rates of oxidation–reduction reactions. It has been shown previously that the accelerating effect of halides on the ferric–stannous reaction is correlated with the oxidizability of the halide used.[2] It is possible that in such reactions, the anion should be closely bound to the oxidizing agent in the activated complex in order for it to be effective. Unlike ferric ion, cobalt undergoes complexing reactions which are, as a rule, much slower than its reductions. For reductions of the type which are accelerated by anions, the activated complex would be in equilibrium only with the cobalt(III) complexes already containing the proper number of anions. If these ideas are correct, the reductions of cobalt(III) offer the possibility of finding out the geometric requirements of the activated complex.

In this paper, however, we shall be more concerned with the reaction of stannate(II) ion. Surrounding cobalt(III) with ammonia molecules has the effect of insulating it from attack by this reducing agent. In fact, Lewis and Coryell[3] have already pointed out that the activation energy for the exchange reaction between hexamminecobalt(III) and hexamminecobalt(II) is much higher than that expected from the charge repulsion alone. In our case, it turns out that the reductions of hexamminecobalt(III) and hydroxypentamminecobalt(III) depend not at all on the cobalt concentrations, and the rate-determining steps are concerned only with stannate(II) ion. Since we have little information about the behavior of basic solutions of metal ions, the kinetic behavior of stannate(II) ion is of additional interest.

Before describing the experiments and their results, we should say that the experimental error present is higher than that ordinarily expected in kinetics investigations because of the difficulty of duplicating results when working with strongly basic solutions. We have tried to find out only the orders of the reaction with respect to the several reactants, and little significance is to be attached to the absolute magnitudes of the constants reported.

Experimental Part

Materials.—The hexamminecobalt(III) chloride used was prepared as described in reference 4. The solid salt was purified by twice recrystallizing from water. Solutions were made by dissolving the salt in concentrated ammonium hydroxide, since fairly high amounts of ammonia had to be present in the runs and this was a convenient way of adding it. The solutions were analyzed for cobalt by electrolytic deposition on platinum. The stannate(II) solution was prepared by dissolving about 50 g. of $SnCl_2 \cdot 2H_2O$ in 100 ml. of water in a 500-ml. volumetric flask. To the milky suspension of the hydrolyzed salt was then added 150 ml. of concd. ammonium hydroxide followed by 250 ml. of 5 M sodium hydroxide solution. After standing a few days, all remaining suspended matter settled out and metallic tin was deposited until equilibrium was reached. The solution prepared in this manner was found to be reasonably stable and easily duplicated. It was standardized on the day of each series of runs by titration with standard ceric sulfate. An approximately 5 M solution of sodium hydroxide was

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