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Adsorption
and
Collective
Paramagnetism



Preface

My purpose in writing this book is to describe a novel method for studying chemisorption. The method is based on the change in the number of unpaired electrons in the adsorbent as chemisorption occurs. The method is applicable to almost all adsorbates, but it is restricted to ferromagnetic adsorbents such as nickel, which may be obtained in the form of very small particles, that is to say, to ferromagnetic adsorbents with a high specific surface. While almost all the data used illustratively have been published elsewhere this is the first complete review of the subject.

The book is addressed primarily to readers interested in heterogeneous catalysis and related areas of surface chemistry, surface physics, and physical metallurgy. For that reason there are included a number of definitions, and an elementary introduction to magnetism. But it is hoped that specialists in magnetism and solid state physics may also find here something of value. For that reason there is included an introduction to adsorption phenomena. If one group finds the detailed magnetic descriptions and calculations to be tedious it is to be hoped that the adsorption work will be found comprehensible, and *vice versa*.

The book was read in manuscript by Dr. Robert P. Eischens and several of his associates, and by Dr. C. A. Neugebauer as well as by his colleagues Dr. Charles P. Bean and Dr. I. S. Jacobs, all of whom made suggestions for correction and amplification. I am indebted also to Dr. Dirk Reinen and to Dr. Y. Yasumori who read the book in proof and who made numerous suggestions for improvement. It is a pleasure to acknowledge the part played by the various graduate students and post-doctorates who contributed to the discovery and development of the methods described. I trust that their respective contributions are adequately recognized at appropriate places in the text.

No list of acknowledgments would be complete without reference to the help received under contract and grant from the Office of Naval Research, the Office of Ordnance Research, the Signal Corps

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P. W. S.

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CHAPTER I

Chemistry of Solid-Vapor Interfaces

1. Introduction

If a surface is exposed to a vapor, molecules of the vapor may adhere to the surface. If this adhesion involves some kind of electronic interaction, the process is referred to as chemisorption. But if no such interaction occurs, the process is called physical, or van der Waals, adsorption.

Until recently there were no very satisfactory methods for studying, or even for recognizing, the occurrence of electronic interaction between adsorbent and adsorbate. There arose, consequently, a tendency to use the term chemisorption for examples of adsorption in which the heat liberated is in excess of about 10 kcal/mole of adsorbate. Physical adsorption was said to occur for cases in which the heat of adsorption is about one order of magnitude less, that is to say, about the same as the latent heat of vaporization of the adsorbate.

There are difficulties in connection with these definitions of chemisorption and physical adsorption. For many systems which obviously involve chemical change, and hence electronic interaction, the heat of adsorption diminishes with increasing surface coverage. Although the reasons for this important phenomenon remain obscure, it is almost certain that chemisorption may occur under circumstances where the heat of adsorption is less than 5 kcal/mole; and evidence has been presented to show that *endothermic* chemisorption may occur. Conversely, there is evidence that in some cases, as of vapors taken up by zeolitic adsorbents, the apparent heat of adsorption (or desorption) is substantially in excess of the latent heat of vaporization, even though other evidence suggests that nothing more than physical adsorption is taking place.

Prior to about 1955 the chief emphasis in studies of adsorption processes was on obtaining kinetic and thermodynamic data, by analysis of which a substantial number of theoretical and practical advances became possible. But since that time attention has shifted to new physical methods which give us more direct insight concerning certain aspects of the over-all adsorption process. So far as the study of useful catalysts is concerned, the two physical methods which have thus far produced most information, and which give promise of producing much more, are the method of infrared absorption spectroscopy as applied to adsorbed molecules, and the magnetic method as applied to ferromagnetic adsorbents.

It is the purpose of this review to present in detail the present status of the magnetic method. The primary objective of this method is to provide answers to the following questions: First, what happens to the adsorbed molecule? Second, what kind of surface bond is formed? And third, what happens to the adsorbent? Such an objective needs no apology. These questions and their answers are of major importance in heterogeneous catalysis, in corrosion, in lubrication, in chromatography, and wherever one surface meets another.

2. The Nature of Chemisorption

The magnitude of the heat of adsorption is only one of several criteria by reference to which we may compare physical adsorption with chemisorption. In this section we shall consider other characteristics peculiar to, or at least more pronounced in, the one as opposed to the other.

It will be noted that physical adsorption is a phenomenon which is related to the boiling point of the adsorbate under the pressure prevailing near the surface of the adsorbent. Physical adsorption is negligible except at temperatures near or below the boiling point of the adsorbate; but chemisorption may have a more complicated dependence on temperature. There appear to be well-established cases, as of hydrogen on nickel, in which chemisorption is unimportant at quite low temperatures, reaches a maximum at intermediate temperatures, and diminishes once more at higher temperatures. Certainly it may be said that chemisorption often occurs at temperatures far above those at which appreciable physical adsorption may be detected.

Physical adsorption is often stated (probably erroneously) to be independent of any specific action on the part of the adsorbent. That is to say, in this view the total volume of vapor which may be taken up by any adsorbent depends, in the case of physical adsorption, solely on the temperature and on the total available surface of the adsorbent. But the situation for chemisorption is quite different—specific activity of the adsorbent is the rule rather than the exception. In proof of this statement it is sufficient to point out the strong chemisorption of molecular hydrogen by some metals, of which nickel is one, as contrasted with the negligible adsorption of hydrogen by copper under identical experimental conditions.

It will be noted also that it is quite doubtful if chemisorption may ever proceed beyond the stage of a monolayer of atoms or molecules, as the case may be, on the surface. But for physical adsorption multilayer adsorption is not only possible but will always occur as the pressure of the vapor phase adsorbate becomes appreciable. It will, of course, be clear that physical adsorption may, and frequently does, occur over a chemisorbed monolayer, provided that experimental conditions are appropriate.

It is not infrequently stated that physical adsorption is a rapid process but that chemisorption may be slow. This is a criterion which must be approached with caution. The rate of physical adsorption may, it is true, be limited only by the rate of diffusion to the surface. But if that surface is less accessible by reason of, for instance, being inside a pore of molecular dimensions, then not only will the apparent rate of adsorption be diminished, but Knudsen flow may render the rate almost imperceptible. There is, on the other hand, a mass of evidence tending to show that chemisorption requires, or may require, an activation energy. This implies that the rate of chemisorption should be measurable. Unfortunately, we know so little about the chemisorption process that it is still impossible to say categorically that all chemisorption must involve an activation process. Certainly there are cases in which true chemisorption (as shown by unquestionable electronic interaction) doubtless occurs but for which no rate has been measured. It is the custom to speak of these as "nonactivated" chemisorption, but whether this distinction is valid remains to be seen. It seems to this writer that too frequently the rate of a

straightforward "old-fashioned" chemical reduction, as of manganese dioxide by hydrogen, has been needlessly interpreted in terms of an activated adsorption.

Fortunately there are some criteria in which one may have more than a little confidence.* If it may be shown that an adsorbed molecule has suffered some chemical change, such as occurs in the hydrogen-deuterium exchange reaction, or in the self-hydrogenation of ethylene on nickel, then it is difficult to escape the conclusion that some electronic interaction of adsorbent and adsorbate, and hence chemisorption, has taken place. The strictly "chemical" approaches continue to be among the most powerful methods at the disposition of the investigator. To these we may add some physical methods, especially infrared absorption spectroscopy, which make it possible to gain direct information concerning the structure of adsorbed molecular species. There have also been developed methods, of which the magnetic method is one, which make possible direct observations on the electronic state of the adsorbent and on the number and nature of the chemisorption bonds. In true chemisorption there must always be some structural change in the adsorbed molecule and there must always be some change in the electron distribution in the adsorbent. In favorable cases these changes may both be observed, and both are subject to quantitative investigation. It may be said that changes such as these also occur during physical adsorption processes. This is correct, but in physical adsorption the magnitude of the changes is trifling as compared with those in true chemisorption.

3. Experimental Methods in Surface Chemistry³

In this section we shall review several experimental methods which are available for elucidating the mechanism of adsorption. The plan will be to describe the method briefly and to state the kinds of information which it provides. Our purpose in this is to provide some background for comparison of the information obtainable by the magnetic method with that from other methods. If some searching techniques have been slighted, the reason is that they do not yield results with which we may directly compare the

* Although perhaps a little less than formerly. De Boer¹ refers to a remarkable example in which mercury isotopes in the two aromatic complexes $\text{Ar}'\text{—Hg—Ar}'$ and $\text{Ar—Hg}^*\text{—Ar}$ were found to exchange without the formation of mixed complexes.²

conclusions based on the changes of magnetization to be described in later chapters. The references given in connection with this section will, in almost every case, be restricted to review articles.

It may seem odd that we start by referring to a purely theoretical approach to the problem. But no account of adsorption can now be complete without at least a passing reference to wave mechanics⁴ and electron theory⁵ as applied to the surface bond. The problems involved, particularly in connection with the former, are indeed formidable. But these methods may ultimately yield the answers which experimental methods have not been able to provide.

The first of the truly experimental methods to be mentioned are those involving adsorption equilibria and the rates of their attainment.^{6,7} These are among the oldest and most fruitful of pursuits in surface chemistry. The experiments consist of volumetric (or occasionally gravimetric) measurement of the quantity of vapor sorbed, at several pressures and temperatures. Such equilibrium studies make it possible to find the surface area of the sorbent and the heat of sorption, or to gain information concerning such molecular processes as may occur on the surface. In recent years studies on the energy of adsorption and lateral interaction have become increasingly sophisticated.

Physical adsorption is not without effect on the physical properties of the adsorbent. This is true in, for instance, the perceptible dimensional changes in porous glass during the adsorption of inert gases,⁸ and in the small but measurable changes in the contact potential of metal films caused by adsorbed argon.⁹ It is also true that the adsorbent may affect the structure of the adsorbed layer or layers. But, in general, the information derived from thermodynamic and kinetic studies of physical adsorption processes will prove to be of minor importance for our main purpose.

When we go to chemisorption the situation is just the opposite.¹⁰ A wealth of experimental data shows that the heat of adsorption is related to the strength of the adsorbent-adsorbate bond, that it generally diminishes with increasing surface coverage, and that these phenomena are both of prime importance in heterogeneous catalysis. Many attempts have been made to relate the activation energy of adsorption to the kind of chemical change required to complete the adsorption process. Many examples of chemisorption are dissociative in nature, and the heat of dissociation is often

indicative of the kinds of dissociation which are thermodynamically possible; the form of the adsorption isotherm is different for different modes of adsorption. Dissociative adsorption (as of molecular hydrogen) into two molecular species, both of which are adsorbed, involves reaction between a vapor molecule and two (or in some cases more) surface sites, while dissociative adsorption (as of nitrous oxide) may yield one species which is adsorbed and one which is not. Similarly, while one species may react with another on the surface, lowering the temperature may halt such reaction and make it possible to estimate the surface coverage produced by dissociation, or even fragmentation, of an adsorbed molecule. From considerations such as these we may gain much information, and we shall make frequent reference to such methods later.

The related, and potentially useful, method of accommodation coefficients¹¹ has not yielded results of major importance, but this is perhaps due in part to the difficulty of precise measurement.

A careful study of reaction products,^{12,13} including the use of isotopes, is still a method of prime importance to surface chemistry, and this is true in spite of the development of powerful physical methods. In fact it is a tribute to the older methods that few surprises have emerged from the application of sophisticated modern techniques. The fact that hydrogen and deuterium may suffer exchange on a catalyst surface is certainly strong (if not quite conclusive) evidence establishing rupture of the hydrogen-hydrogen bond through the agency of the surface. Equally significant is the formation of ammonia from molecular hydrogen plus molecular nitrogen. To such relatively simple examples we may add many others, some of which, involving complicated arguments relative to the stereochemistry of the adsorbate, reveal possible modes of adsorption and interaction through study of the reactions of exchange, isomerization, and the like.^{14,15} One of the most useful of such techniques (for our present purposes) is the refinement by Kemball¹⁶ of deuterium exchange for determining the number of dissociated hydrogens per molecule of adsorbate. Cyclohexene is, for instance, chemisorbed in the room temperature region on nickel by dissociative adsorption leading to the formation of two nickel-hydrogen bonds per molecule of cyclohexene. The information thus obtained lends itself readily to direct comparison with the magnetic method under conditions which appear

to be identical. The agreement, as we shall in due course see, is gratifying.

We turn now to the physical methods, some of which give information concerning the adsorbed molecule, and others of which give information concerning such changes as may have occurred in the adsorbent. Some methods give a measure of information relative to both adsorbent and adsorbate simultaneously. We shall group together electron microscopy and electron diffraction. In recent years electron microscopy has reached surprising limits of resolution, but thus far the limit still lacks about one order of magnitude for our purpose.

The method of electron diffraction extends the limit of resolution.^{17,18} It is true that we are restricted to rather specialized conditions. These include quite high vacuum* and extraordinary care to obtain clean surfaces. But it is possible to use single crystals with relatively large, defined faces. Under these conditions, and with low-speed electron beams, one may "observe" adsorbed molecules and make useful interpretations concerning their mode of attachment and their distribution on the surface. In favorable cases it is possible to draw some conclusions concerning the mutual reactions of adsorbed molecules. We shall not have many occasions on which to compare low-speed electron diffraction data with the magnetic method, but we shall have some.

The method of infrared absorption spectroscopy¹⁹ is, for our purposes, in quite a different category (see Fig. 1). We shall examine the method in some little detail. At first glance it would appear to be impracticable to observe the absorption spectrum of a monolayer of adsorbed molecules; but under favorable conditions this may be done. The restriction is that the adsorbent must be present in very small particles, that is to say, with a high specific surface. This is a definite advantage because it places the method in the class of using the same, or similar, samples as those to which we shall have reference in the magnetic method. The underlying reason for this is obvious. We are attempting to measure the properties of an adsorbate which is inevitably present in rather small proportion relative to the adsorbent. In order to obtain a useful signal we must make the proportion of adsorbate as large

* We shall use the term "high vacuum" to mean pressures substantially lower than 10^{-6} mm Hg.

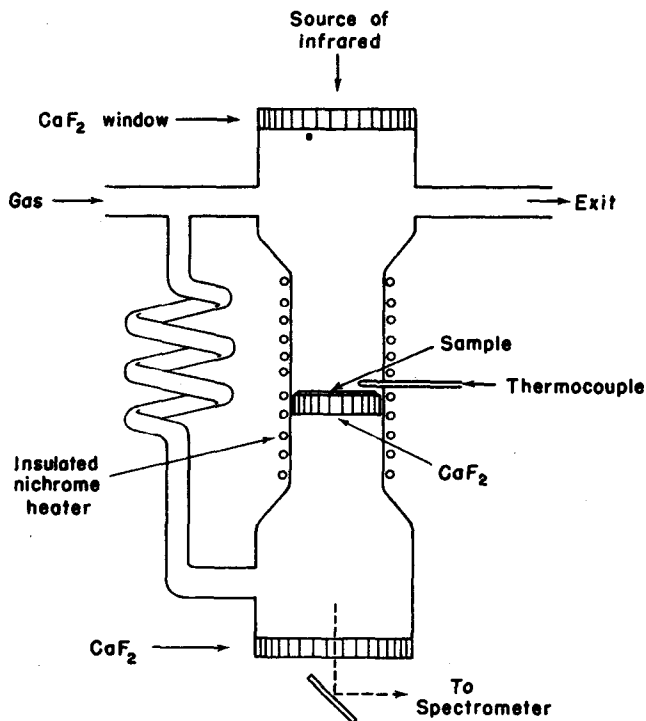


FIG. 1. Cell used for observation of the infrared absorption spectrum produced by molecules adsorbed on metals and oxides of interest in heterogeneous catalysis (after Eischens).

as possible and this may only be done by enlarging the specific surface of the adsorbent. Inasmuch as this is also the condition required, more often than not, for efficient catalysis, we find the method of absorption spectroscopy, together with the magnetic method, to be almost unique among the physical methods in their ability to deal with practical catalysts.

The infrared absorption spectrum of adsorbed molecules is obtained as rather poorly defined, but nevertheless recognizable bands (see Fig. 2). These are observed by passing the beam through a thin deposit of supported catalyst, as of nickel on silica gel; the total mass of metal adsorbent being only a fraction of a milligram. Various gaseous adsorbates may be admitted to the sample. The relatively large dead-space must be kept at low pressure, and it is obviously difficult to make a very accurate estimate of the

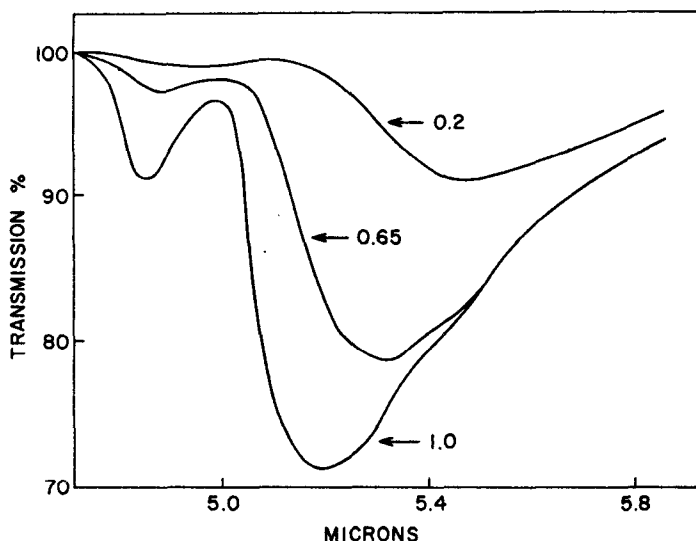
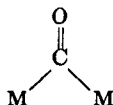


FIG. 2. Infrared absorption bands of carbon monoxide adsorbed on platinum at several levels of surface coverage, as indicated (after Eischens and Pliskin).

amount of vapor actually taken up.

The absorption bands are identified, for the most part, by comparison with the known spectrum of gaseous molecules. It is, for instance, known that the carbon-oxygen stretching frequency in carbonyls produces a band at 4.9 microns for "linear" $M=C=O$ systems, but at 5.3 microns for "bridged" structures, as shown below. Both of these are found in carbonyls such as $Fe_2(CO)_9$.



The observation of bands at these frequencies is taken as proof of the mode of attachment of the chemisorbed molecule.

The method has yielded a wealth of interesting information. We shall see later that the method yields results which are sometimes not in complete agreement with those from other methods. A criticism sometimes heard concerning the absorption spectrum method is that the bands associated with a group in a vapor phase molecule should not necessarily be the same as the bands in a

group attached to a metal atom which is itself part of a metal surface. To give a specific example—is it correct to say that the bands associated with a C—H group in ethylene are necessarily the same as those for the same group when the carbon is not only attached to a nickel atom, but when that nickel atom is itself part of the complicated system found at a metal surface?

These remarks should not be construed as a general criticism of what has proved to be a powerful tool in surface chemistry.²⁰ Rather they are meant to show one possible direction in which we may look in an effort to reconcile a few discrepancies. Concerning these we shall have more to say later.

The measurement of magnetic susceptibility of an adsorbed gas is a method which, in the hands of a few devoted followers, has yielded useful results.²¹ The method consists of measuring the susceptibility of an adsorbent before and after admission of a gas which may be taken up by the surface of the adsorbent. The method is, in general, restricted to paramagnetic gases such as oxygen or nitric oxide because these are the only adsorbates which might be expected to show measurable changes of susceptibility after adsorption. In this way it is possible, for instance, to follow the conversion of paramagnetic molecular oxygen to diamagnetic oxygen while it is adsorbed on graphite.

It is doubtful if this method could be refined to a degree such that it would be sensitive enough to detect changes in diamagnetic molecules. Actually there is no particular reason for attempting such an improvement in sensitivity because the same purpose is achieved, with vastly improved precision, by the study of nuclear magnetic resonance in adsorbent-adsorbate systems. The information so gained is related chiefly to the electronic environment of protons in, or derived from, the adsorbate.

These magnetic susceptibility methods should not be confused with those in which the magnetic changes occur in the adsorbent. These latter form the principal subject of this review.

We turn now to those methods in which attention is directed primarily to the adsorbent rather than to the adsorbate. The field-emission microscope actually belongs to this class because it uses changes of work function; and the first method to be described below, that of surface dipole measurement, certainly belongs to both classes.

Adsorption of a molecule on a surface creates a surface dipole

which may be measured with fair precision, and the sign and magnitude of which give some information concerning the mechanism of adsorption. The surface dipole is related to the work function and, in the classical work of Langmuir, was measured simply as the change of contact potential between two wires, one of which serves as a thermionic emitter.

Methods currently in use for the study of the several electron-emission and surface potential phenomena include modifications of the original Langmuir method, the field-emission microscope, photoelectric methods, and a variety of methods which, directly or indirectly, measure the contact potential difference between a surface under investigation and a reference surface.²² For our purposes the most useful methods are the photoelectric work function method (see Fig. 3) and the capacitor method. In the former

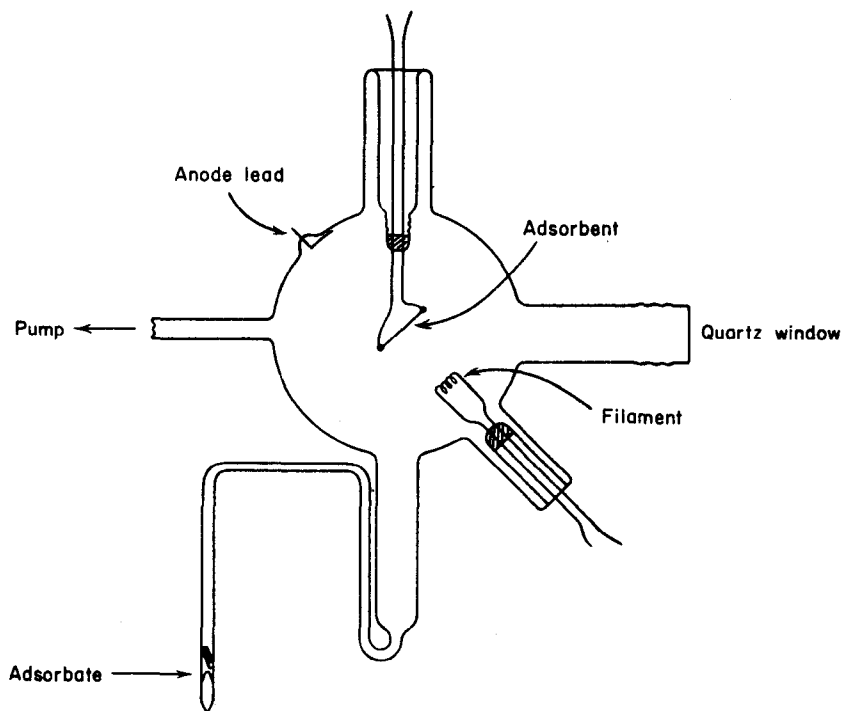


FIG. 3. Apparatus for measuring the change of photoelectric work function caused by an adsorbed vapor. The filament is used to produce the adsorbent film (after Suhrmann).