MODERN TECHNIQUES FOR INVESTIGATING INTERACTIONS WITH SURFACES

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I. Introduction

Basic research on the nature of surfaces, with accompanying important applications in the fields of corrosion, lubrication, adhesion, and detergency, to mention only a few, has been advanced by the development of several new techniques. These include the field emission microscope to pursue the interactions of molecules with metal single crystals, infrared spectroscopy applied to interactions at surfaces while chemical changes are actually taking place, calorimetric measurements of the heats of immersion of powders into liquids, and nuclear magnetic resonance also to study the state of adsorbed species.

In order to appreciate the present full impact of these four new tools, the current state of affairs in the field of surface chemistry will be reviewed first. Particular emphasis will be placed on metal surfaces; not only has much of the previous theoretical and experimental work, but also two of the new tools, the field emission microscope and infrared spectroscopy, have been directed mainly at metals. The surfaces of dielectrics such as bulk oxides and salts will be discussed briefly; it will be shown later that the other two new tools, heat of immersion and nuclear magnetic resonance techniques, have provided particularly fruitful approaches to the study of interaction with these materials. Also included are a few reactions at cell walls, one of the most complicated types of surfaces, as examples of an area where the life scientist and the surface chemist are welding their disciplines.

II. Present Status of Surface Chemistry—a Survey

This survey is divided into four parts: interaction energies derived for ideal cases, surface heterogeneities which complicate the classical estimations of these energies in real cases, the problem of whether various interactions should be classed as physical adsorption or chemisorption, and two examples of technological applications of surface chemistry. One of these latter examples is to the field of corrosion, while the other deals with several specific types of interactions with cell walls.

A. INTERACTION ENERGIES

1. Energy of interaction between isolated nonpolar molecules

As a molecule approaches a solid surface, it begins to interact with the unit building blocks of the solid, whether atoms or ions; interactions with units thirty to fifty diameters away in the surface and deep into the bulk must be taken into account. The present ability to estimate the sum of these interactions rests on the knowledge of the interactions between two isolated atoms, molecules, or ions.

The forces of attraction and repulsion arise from the interaction of the fluctuating electrical particles of which atoms or molecules are made. When nonpolar molecules interact, the forces of attraction are nonpolar van der Waals forces. They are sometimes referred to as dispersion forces, since London (73) showed the close connection between their nature and optical dispersion. The interaction energy, E_w, is represented as follows:

$$E_w = -\frac{A_1}{r^6} - \frac{A_2}{r^8} + \frac{R}{r^n}$$

where A_1, A_2, R = constants depending on the nature of the atom,
r = distance of separation,
A_1/r^6 = attraction term due to dipole–dipole interaction,
A_2/r^8 = attraction term due to dipole–quadrupole interaction, and
R/r^n = repulsion term.

Attraction terms involving exponentials in r greater than 6 or 8 can usually be neglected. In the repulsion term, due to the mutual interpenetration of electron clouds, n is usually taken to be 12, but may differ considerably from that value. On quantum-mechanical grounds, Born and Mayer (25) arrived at an exponential form for this term.

The forces of attraction and repulsion balance at an equilibrium distance $r = r_0$ such that $(\partial E/\partial r)_r = r_0 = 0$, so that the coefficient R can be eliminated:

$$E_{r0} = -\frac{A_1}{2r_0^6} - \frac{A_2}{3r_0^8} \tag{2}$$

where r_0 = equilibrium distance. When A_2 is taken to be zero, this equation reduces to:

$$E_{r0} = -\frac{A_1}{2r_0^6} \tag{3}$$

If equation 1 is put in terms of E_{r0}, r_0, and A_1, curve a in figure 1 is obtained for $A_2/A_1 = 3 \times 10^{-16}$ [adapted from Honig (61)]:

$$E_w = E_{r0}\left[2\left(\frac{r_0}{r}\right)^6 - \left(\frac{r_0}{r}\right)^{12}\right] \tag{4}$$

If A_2 is taken to be zero, the minimum representing the magnitude of the attractive energy at the equilibrium distance would be shallower by about 0.1 kcal./mole. This second attractive term arises from fluctuating dipole–dipole interactions; in some cases, but not usually, this second contribution may be greater than the first. It should also be noted that in estimations of interaction energies the repulsion term and the second attraction term often have been considered just to counterbalance each other.

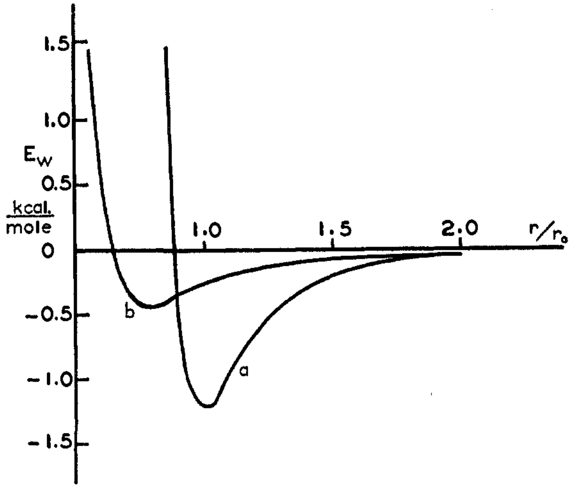

FIG. 1. Energies of interaction with relative distance apart. Curve a, between two atoms; curve b, between an atom and a uniform covalent surface. Adapted from Honig (61); reproduced by permission of the New York Academy of Sciences and the author.

2. Nonpolar molecules with uniform covalent surfaces

To proceed from the interaction of two isolated molecules to the situation for the mutual interaction of molecules with metals, an intermediate step must be taken through interaction of a nonpolar molecule with a uniform covalent surface.

Both dispersion and repulsion forces are additive as a first approximation (74, 75). The addition must be performed pair-wise over all pairs between the adsorbate and each lattice atom of an ideal covalent crystal. As Polanyi and London (89) first showed, however, this tedious procedure can be replaced by an integration process. These authors used only the first attractive term and obtained:

$$E_w = -\frac{\rho\pi A_1}{6r_0^3} \tag{5}$$

where ρ is the number of atoms in each cubic centimeter of the adsorbent. Hill (38, 59, 60) included the repulsion energy but set A_2 equal to zero to obtain:

$$E_w = \pi\rho E_0 r_0^3\left[\frac{1}{3}\left(\frac{r_0}{r}\right)^3 - \frac{1}{45}\left(\frac{r_0}{r}\right)^9\right] \tag{6}$$

which is plotted as curve b in figure 1.

Here r is the perpendicular distance from the surface and r_0 is the equilibrium distance of the adsorbed molecule from the surface. Even though this minimum is shifted to the left from the minimum for the interaction curve for two molecules, the actual distance from the surface atom may be greater. Honig (61) extended this development to include the quite small correction provided by neglect of the A_2 term. If interaction is added for adsorbent atoms up to some distance away and then the integration is used for the remaining contributions, de Boer (15, 19) has shown that higher and probably more correct values are obtained.

3. Conducting surfaces

(a) Interactions with nonpolar molecules

When a nonpolar adsorbate approaches a conducting surface, van der Waals forces must be modified to handle increased repulsion. As shown by Margenau and Pollard (76), the metal cannot be treated as ideally polarizable. The dipoles of a nonpolar adsorbate fluctuate too rapidly for the conduction electrons in the metal to keep up with them. Two terms arise, one from the polarization of the metal and the other from the polarization of the adsorbed molecule. The first term leads to a positive contribution representing repulsion. Nevertheless, as before, the total energy of interaction E_w is inversely proportional to the third power of the distance.

Usually, a more important interaction between a nonpolar atom or molecule and a conducting surface is provided by the dipole induced in the adsorbate. Two classical approaches have shown evidence of this effect. The two-dimensional van der Waals equation can often be applied successfully to adsorbate behavior but a striking feature is that the attraction constant a required to fit experimental data for metal adsorbents is either very low or negative. Repulsion between similarly directed induced dipoles would explain this finding. Also, the recent contact potential measurements of Mignolet (79) showed a large change when, for example, xenon was adsorbed on nickel. An induced moment of 0.42 debye with the positive end away from the metal would explain the change in contact potential on adsorption. This contribution can be evaluated (18) from the equation:

$$E_\alpha = -\frac{\mu^2}{2\alpha} \tag{7}$$

where α is the polarizability of the adsorbate and μ is the dipole moment estimated from contact potentials or the van der Waals attraction constant. Both E_w and E_α, it should be noted, are independent of position over the underlying structure of a uniform metal surface.

The mutual attractive forces between adsorbate molecules at temperatures below the two-dimensional critical temperature may lead to two-dimensional condensation (17, 60), as revealed by steps in the isotherm. Examples include the adsorption of a number of gases on graphitic materials or charcoals (44, 84).

The lack of specificity of adsorption with position over a uniform metal surface at ordinary temperatures, even though rough on an atomic scale, implies unrestricted translational and rotational motion. Support for this contention is provided by application of two-dimensional gas equations of state at low coverages, as mentioned earlier, and investigations of entropy changes on adsorption (22, 66, 68).

The chief difficulty with the entropy studies is that the *total* estimated entropy change on adsorption is ascribed to the adsorbate. Yet the adsorption process requires that the adsorbent also be perturbed. The original outer layer on an ideal metal surface is as much as 0.2 A. further from the second layer than bulk distances would suggest (98, 107). Entropy changes then occur owing to adjustments as the adsorbed film builds up. Measurements on charcoals (6, 7, 78) and silicas (113) have indicated accompanying volume changes, but no such results have yet been reported for metals. That the contribution of surface perturbations to the total entropy change may be exceedingly large is shown by studies of adsorption of water on kaolin in this laboratory; if all the entropy change is allotted to the water, its entropy would inconceivably be below zero.

(b) Interactions with polar molecules

Both polar molecules and ions interact with conducting surfaces in a way that is best described in terms of image forces. That is, an electric charge of opposite sign may be considered to form below the surface at a distance equal to that between the actual inducing charge and the surface.

Since the image force for an ion is:

$$F_i = \frac{n_i \epsilon^2}{(2r)^2} \tag{8}$$

where ϵ is the electron charge, n_i is the ionic charge, and r is the distance between the ion and the metal surface, the contribution to the adsorption energy is:

$$E_i = \int_{\infty}^{r_m} \frac{n_i \epsilon^2}{4r^2}\,\mathrm{d}r = -\frac{n_i^2 \epsilon^2}{4r_m} \tag{9}$$

A long-standing problem met here is to locate the exact boundary of the surface. Two major possibilities are the periphery of the surface atoms and the plane through their centers. In the case of ideal polarizability, the better fit with experiment seems to be reached (16) when the boundary is drawn through the centers of the surface atoms, but when electron transfer occurs, the effective boundary appears to be the periphery.

The energy of interaction of a dipolar molecule with a conducting surface is also dependent on an image force such that:

$$E_\mu = -\frac{\mu^2}{16 r_m^3}(1 + \cos^2\theta) \tag{10}$$

where μ is the dipole moment and θ is the angle between the direction of the dipole and the normal to the surface. This contribution is low and in most cases may be neglected.

Unless the adsorbate is an ion, the foregoing analysis shows that the most important contribution to the adsorption energy on a uniform metal surface is due to an induced dipole. This is likely to be true even for molecules possessing modest permanent dipoles, such as carbon monoxide, or for those possessing quadrupoles, such as nitrogen.

4. Dielectric surfaces

As was the case with conducting surfaces, the interaction energies with dielectric surfaces such as salts and oxides depend on the nature of the approaching molecule. However, the situation with conducting surfaces, where the dominating force is due to polarization of the adsorbate, is sharply distinguished from that with dielectric surfaces, where van der Waals forces and dipolar forces excel.

(a) Interactions with nonpolar molecules

The preponderance of the interaction of a nonpolar adsorbate with a dielectric surface is due to ordinary van der Waals forces. For example, considering the (100) face of a face-centered cubic crystal like sodium chloride, the greatest interaction occurs with the site in the middle of the square array of charged ions rather than over the individual ions or directly between them (83, 114). In the physical adsorption of an atom of a rare gas, the difference amounts only to a few hundred calories in 1 to 3 kcal. Calculated and experimental heats of adsorption on uniform faces agree well (86). Most powders, however, are not uniform; with polycrystalline mixtures, equal proportions of the common (100), (110), and (111) faces are often presumed to be present for purposes of estimation.

Calculations which have been made for gases interacting with ideal ionic lattices have been capably summarized by Honig (61). One of the chief inadequacies of these estimations versus reality is that account is not taken of the overlapping of the orbitals of the ions which make up the solid. This smoothing out of the electric fields is now receiving deserved attention from several directions. It has been emphasized, too, that in dielectric solid surfaces the outermost layer of ions is at a shorter distance from the second layer than bulk distances would suggest (1, 93). Also, as Verwey (107) and Weyl (110) have concluded, the positive and negative ions are staggered in the surface, with the negative ions displaced outward. To put the matter in Weyl's terms, the negative ions with their extra electrons are more easily polarized so that they can more readily accommodate themselves to the unbalance of forces at the surface. These factors remain to be included in the calculations in order to make the theoretical calculations secure.

The quadrupole moment of nitrogen, Drain has indicated (35), is probably responsible for its usual higher heats of adsorption on ionic crystals over that for oxygen or argon. Nitrogen goes down so gradually but definitely on dielectrics as the pressure is raised that when essentially the first layer has formed, the plateau in the adsorption isotherm (amount adsorbed versus pressure) allows the amount required for the first layer to be estimated. Alternately, the B.E.T. equation (27) can be used to calculate the number of molecules required to complete one layer. From a known value for the area of each nitrogen molecule, usually assuming close-packing, the surface area (per gram) can be calculated.

(b) Interactions with polar molecules

The energies due to repulsion and to nonpolar van der Waals forces have already been discussed. If ions are adsorbed on an ionic lattice, the contribution due to Coulomb forces is very small, owing to counterbalancing by ions of the same sign in the surface. In fact, for mono-monovalent salts, the energy contribution is only 6.6 per cent of that for separated ions. The most important contribution on uniform surfaces is due to polarization of the dielectric:

$$E_{\epsilon,\alpha} = \frac{n_i^2\epsilon^2}{4r_0} \cdot \frac{K-1}{K-2} \tag{11}$$

where K is the static polarizability of the dielectric.

Polar molecules interact with ionic crystals in proportion to their dipole moment μ according to the equation:

$$E_\mu = -F\mu \tag{12}$$

It will be shown that F, the electrostatic field emanating from the solid, can be estimated for various ionic solids through measurements of heats of immersion. This contribution is large for highly polar molecules like water. Polarization of the adsorbate by the dielectric, however, contributes a small amount even if the molecule is nonpolar.

B. SURFACE HETEROGENEITIES

In the preceding section it was shown that great progress has been made in deriving equations from which interaction energies may be calculated for uniform surfaces. In practical circumstances, however, surface heterogeneities make the application of classical energies either vastly difficult or impossible. There are three major types—physical, chemical, and induced. A special complication arises from the omnipresent water.

1. *Physical heterogeneities*

(a) Lattice imperfections

A surface is, of course, never entirely smooth on an atomic scale. A more serious problem is usually provided by roughness on a larger scale. Real crystallites are riddled with all sorts of lattice imperfections such as fissures, elevations, and lattice dislocations. Figure 2 presents a schematic diagram of some of the possibilities. Physically bound molecules are more energetically held in crevices than in step positions, than on plane surfaces, than on edges or corners. The

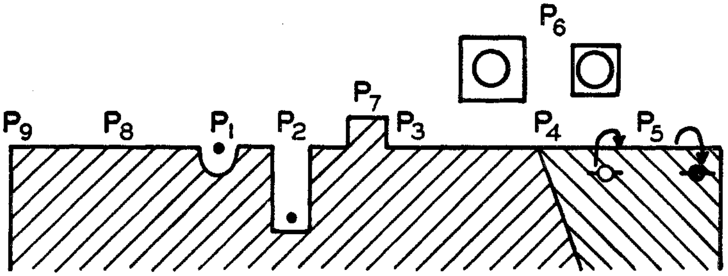

FIG. 2. Schematic diagram of surface heterogeneities. The numbers indicate the order in which the positions are rated for energy. Physically bound molecules are more energically held by P_1; in chemisorption, on the other hand, P_9 has the greatest tendency to participate.

reverse of this order applies in chemisorption; here, corners or raised positions commonly have the greatest tendency to participate in electron sharing or transfer.

(b) Differences between planes

Many physical measurements of metals through a single crystal or over different lattice planes lead to the conclusion that properties vary significantly in different directions. For example, a voltage can be applied to the different planes of a metal crystal to measure the energy required to liberate electrons. The most reliable measurements are available for tungsten (72); here the electron work function ϕ varies from 4.3 to 5.5 electron volts. The work function increases with the packing density of the atoms in the various planes and also the specific surface energy decreases linearly with increase in ϕ (101). These findings are expected, but more important for the present discussion are expected differences in adsorbate–adsorbent interactions on different planes.

One of the best examples of directional effects during the physical adsorption on a homogeneous, well-defined crystallographic surface was provided by Rhodin's work (92) on the (100), (100), and (111) faces of a single crystal of copper. Figure 3 shows that at low coverages the isosteric heats of adsorption of nitrogen on the single faces are constant but are higher for the planes with higher packing density. Note that the heat of adsorption rises to the highest maximum on the least densely packed (110) face. Here the dipoles induced in the nitrogen are lowest because the van der Waals attractive forces more readily surmount the repulsive forces between the dipoles as the surface becomes covered

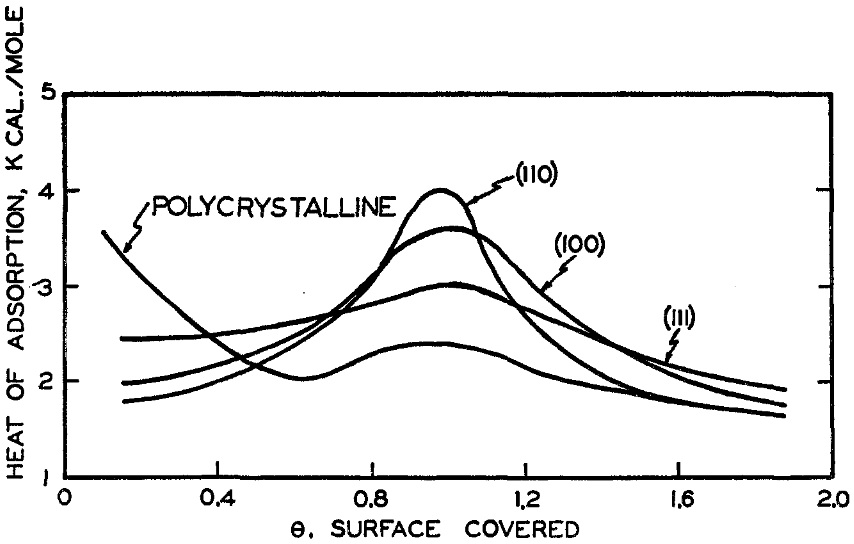

FIG. 3. Isosteric heats of physical adsorption of nitrogen on homogeneous separate faces of copper. The values were calculated from isotherms measured at the temperature of liquid nitrogen on an extremely sensitive microbalance. Adapted from Rhodin (92); reproduced by permission of the American Chemical Society.

with one layer. (The high initial heat on the polycrystalline copper which tends to erase the maximum at one layer is the result of intercrystalline sites; this type of heterogeneity will be discussed in more detail next.) Of the new tools, field emission microscopy provides decisive information on the effectiveness of different lattice planes.

(c) Intercrystalline sites

As Rhodin's work showed, effects of intercrystalline sites on polycrystalline surfaces are readily revealed in adsorption studies. The evidence for this type of heterogeneity is the initially high heat of adsorption, followed by a gradual decrease (rather than stepwise) as coverage is increased. Along a similar vein, work in this laboratory (57) showed that the interaction of argon with polycrystalline molybdenum powder decreases as sintering increases.

Indeed, most commonly used powders are polycrystalline in nature. A classic piece of work to show that the widely used rutile titanium dioxide (both as a pigment and as an oxide adsorbent in academic studies) is heterogeneous even to physical adsorption was provided by Drain and Morrison (36, 37). On the basis of heat capacity measurements of argon (subtracting the heat capacity of the rutile from that of the rutile with adsorbate) at three coverages, the contributions to the configurational entropies were determined to be those shown in figure 4. The configurational entropies are obtained by subtracting from the total entropies the contributions due to internal degrees of freedom. If the ad-

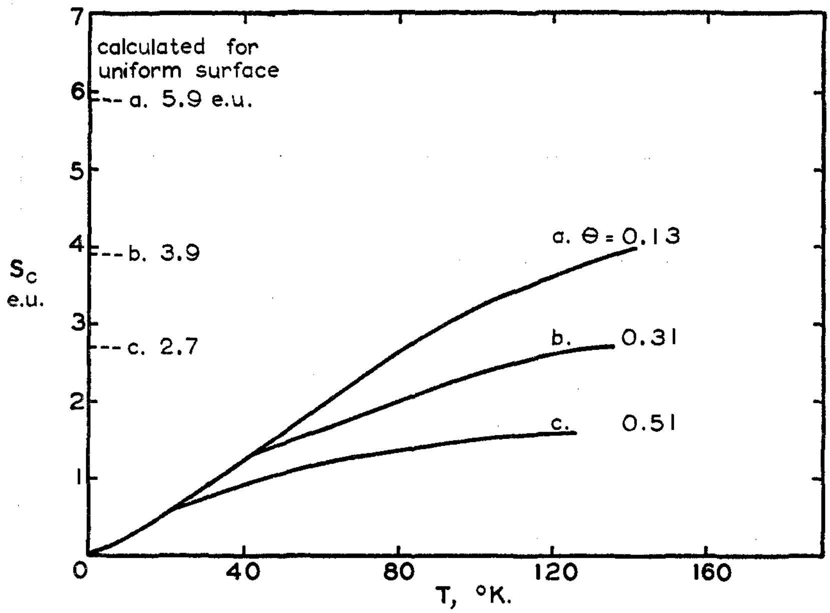

FIG. 4. Configurational entropy of argon on titanium dioxide based on heat capacity measurements. Adapted from Drain and Morrison (36); reproduced by permission of the Faraday Society and the authors.

sorption sites all possessed the same energy of attraction, then there would be a large zero-point configurational entropy because of the many possible ways for the surface to fill; the calculated values for the three coverages are indicated at the left in figure 4. Instead, the entropy curves all extrapolate essentially to zero at zero absolute temperature. The surface is indeed heterogeneous for the adsorption of argon. Of course, the site-energy distribution is likely to differ considerably for different adsorbates.

The rutile sample used by Drain and Morrison no doubt also presented a variety of crystal faces to the adsorbate molecules. The heterogeneity was likewise enhanced, as mentioned earlier, by the differences in interaction energies among the sites on the various faces.

2. Chemical heterogeneities

Chemical heterogeneities arise from impurities which may be highly influential even when present in low concentrations. Often, but not always, impurities migrate to the surface. It is convincing that the congregation at the surface of species active with the adsorbate might easily dominate among the total of 10^{14} to 10^{15} sites per square centimeter even when the concentration is in parts per million.

As an example of the problem that impurities create, surface chemists have been debating for some time whether copper does or does not chemisorb hydrogen. This question has been resolved by showing that really clean copper surfaces will not, whereas if a little oxygen has been previously chemisorbed to rob the metal of some of its electrons and so raise the work function, then hydrogen is readily chemisorbed.

Defect structures due to lattice vacancies, to the presence of interstitial atoms or ions, and to substitution of ions of abnormal valency in the lattice also contribute to the complexity. Vol'kenshteĭn (108) has suggested the valuable concept of the mobility of lattice defects, which helps to explain consequent changes in interaction during the time of observation, particularly at elevated temperatures. Elucidation of the effect of some specific defect structures is provided by the new tools, particularly with heats of immersion and nuclear magnetic resonance.

3. Induced heterogeneities

The first molecule down can have a decided effect on the energy with which the succeeding molecules are adsorbed. In chemical interactions especially, the interaction energy often decreases as coverage increases. In physical adsorption on a homogeneous surface, lateral attraction between adsorbed molecules may lead to increased energy of interaction, as was the case in Rhodin's work.

4. The special problem of water

Water is present in most systems and has profound effects on their nature. On heating calcium fluoride to remove water, for example, a reaction takes place and hydrogen fluoride is desorbed instead of water (20). On further heating the resulting surface hydroxyl groups are converted to surface oxides. A similar behavior is followed by many bulk oxides such as silica, which tend to present surface hydroxyl groups to the surroundings until outgassed above 300°C. or unless exposed to a strong desiccant at perhaps 200°C.; surface silanol groups are converted to siloxane groups which are hydrophobic unless treated to bulk water for long periods of time to reconvert them to hydroxyl groups (67).

Because of its high dipole moment per unit area or unit volume, water tends to be found at dielectric surfaces preferentially to other media in which the solid may be dispersed. Its potent action is sometimes phenomenal. It is well known since the work of Kruyt and van Selms (69), for example, that films of water on starch or glass spheres in hydrocarbons can cause flocculation; the films of water tend to coalesce to reduce the interfacial free energy, as illustrated in figure 5. What has not been recognized until recently (31) is that even trace amounts of water, much less than a monolayer, can be responsible for flocculation and the development of structure in such sols. The few molecules of water present if the dispersion is made under rather stringent aseptic conditions possess sufficient mobility to move to tentative points of juncture, there to form a cementing bridge between the particles. This concept is strengthened by the fact that the addition of a small amount of a strong desiccant such as phosphorus pentoxide or anhydrous magnesium sulfate can destroy the gel structure and make the system limpid.

Additional evidence for the potency of water is provided by its effect on the shifts of color produced when a dye such as *p*-hydroxyazobenzene is adsorbed on dry alumina (17). The adsorbed state is excited because the hydroxyl groups are polarized by the negative oxygen atoms which protrude from the alumina surface; hence the absorption spectrum is shifted to longer wavelengths. If water is added, the organic molecules are displaced and show up in their original yellow color.

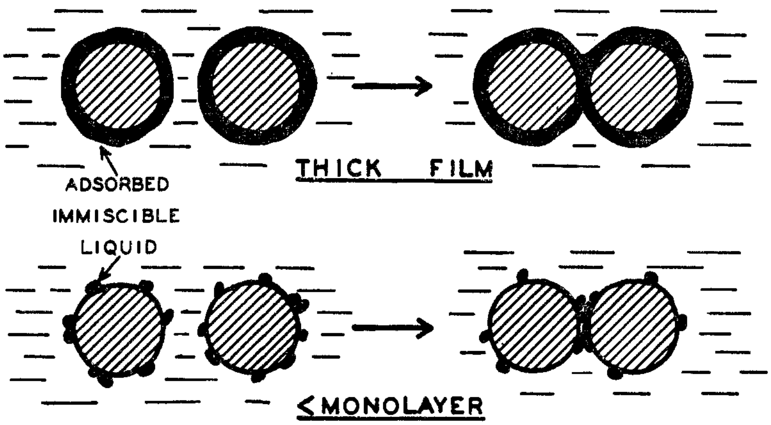

FIG. 5. Flocculation by adsorbed water on hydrophilic solids. Note that the mobility of the water molecules at less than a monolayer also leads to the formation of water bridges. From Zettlemoyer (117); reproduced by permission of the Federation of Paint and Varnish Production Clubs.

Synthetic cracking catalysts for petroleum consisting of minor amounts of alumina incorporated in a silica lattice have the option of presenting Lewis or Brønsted acid sites, i.e., the sites may be simple electron acceptors or they may be protonic in nature. Much effort is being given to the questions of which type predominates and of the acid strengths of the sites. Doubtless their nature depends strongly on the ambient conditions during use; lower temperatures and higher concentrations of water vapor favor the Brønsted type. (The question of the distribution of acid strengths will be considered under heats of immersion.)

These examples serve to indicate that strong precautions must be taken to study interactions involving dielectric surfaces with the water problem under precise control.

C. PHYSICAL ADSORPTION VERSUS CHEMISORPTION

A major problem of the surface chemist is to decide whether the interaction at a surface should be classed as physical or chemical. Theoretically, any interaction leading to changes in the energy states of electrons should be regarded as a chemisorption. Since in many cases energies have not yet been derived from experimental data, it is often impossible to decide with certainty what the nature of the interaction is.

Through studies of changes in work functions and changes in the photoelectric effect caused by adsorption onto metals (64, 72), it has gradually become clear that such surfaces may absorb electrons from, emit them to, or share them with the adsorbate. It has been illustrated clearly by de Boer (14, 24) that the events which do occur depend on the magnitudes of the energy to release electrons from the metal and the ionization energy of the adsorbate atom, together with the adsorption energies. Measurements of heats of adsorption therefore often provide a useful, but not always decisive, approach to determine the extent of the interaction; if rates of adsorption or desorption are also measured, a more certain conclusion can often be reached. Other avenues which deserve attention here are the influences of bulk properties such as electronic structure, magnetic susceptibility, and electrical resistance.

Studies of heterogeneous catalytic reactions have also been often directed to the degree and mechanism of interaction at the surface. This approach can suffer from a number of indirect causes. Adsorption of the several species reacting at the same time or of the products of the reaction can complicate matters. Rate studies to establish the activation energy and frequency factor must involve several temperatures where the adsorption characteristics may differ. For these reasons, catalytic studies will not be included here.

Beyond the study of the bulk properties of the adsorbent, the best criteria for physical adsorption or chemisorption are afforded by changes in the optical, magnetic, or other properties of the adsorbed molecules. Infrared spectroscopy has been successfully employed for adsorption on metals, but little application has yet been made to nonmetals for this purpose.

1. Heats of adsorption

An interaction can sometimes be classed as chemical or physical from the magnitude of the heats of adsorption. Heats below 10 kcal./mole usually result from physical adsorption; this value approaches the value for energy of liquefaction and suggests only van der Waals forces. Heats above 15 kcal./mole usually place an interaction in the chemisorption class, but it must be emphasized that these limits are somewhat arbitrary.

The irreversibility of an interaction is another means for deciding that chemisorption has occurred. But many cases exist where the heat of desorption is of the same magnitude as that for adsorption despite the fact that the interaction is chemical. A case in point is the adsorption of sodium on tungsten. Sodium prefers to be adsorbed chemically as a positive ion, because the minimum energy for the adsorbed ion is lower than for the adsorbed atom. On heating, however, the sodium will be desorbed physically in the atomic form because the energy level for the atom is lower than that for the ion. The heat of desorption is of the same magnitude as for adsorption, so that in this case a reversible concept applies just as in physical adsorption.

In many cases, dissociative chemisorption of molecules such as hydrogen or nitrogen takes place on bare metals. These chemisorptions may or may not involve an activation energy. For hydrogen, for example, it has become increasingly clear that activation energies are low or nonexistent on really pure metal surfaces (10, 94, 95, 103). The chemisorption of nitrogen on tungsten proceeds without an activation energy also, but that of nitrogen on iron involves a definite activation energy. The presence of such an energy barrier would allow the chemisorption to be endothermic as, for example, for hydrogen on glass (23, 65, 71).

A complicating factor is the effect of heterogeneities. These will tend to decrease the heat of adsorption and increase the activation energy as the surface coverage increases. Practically no chemisorption measurements useful to this discussion have been made on single faces of metal crystals. Here is where tremendous advances have recently been made by use of the field emission microscope.

Heats of adsorption can also be used effectively to follow chemisorption of organic substances. In figure 6, the fall in the heat of adsorption with amount of benzene adsorbed on nickel powder is plotted from data developed in this laboratory. The amount physically adsorbed was estimated from the amount irreversibly adsorbed. The heat of adsorption was also measured on an oxidized nickel powder surface, because it was felt that here all the benzene would be physically adsorbed. When the heat values on the oxidized surface were plotted, starting at the end of the chemisorbed amount on the bare surface, they were superimposed over the values for the physically adsorbed portion on the bare surface. In other words, the physically adsorbed benzene molecules on a bare nickel surface behave energetically the same as physically adsorbed molecules on an oxidized nickel surface. Of course, a similar dovetailing with the heat of chemisorbed adsorption can be shown if the heats of adsorption on bare metal surfaces are measured after pumping off the physically adsorbed portion.

A striking discovery by Maxted (77) deserves mention. He showed, as is seen in figure 7, that the initial heat of adsorption of ethyl sulfide is considerably

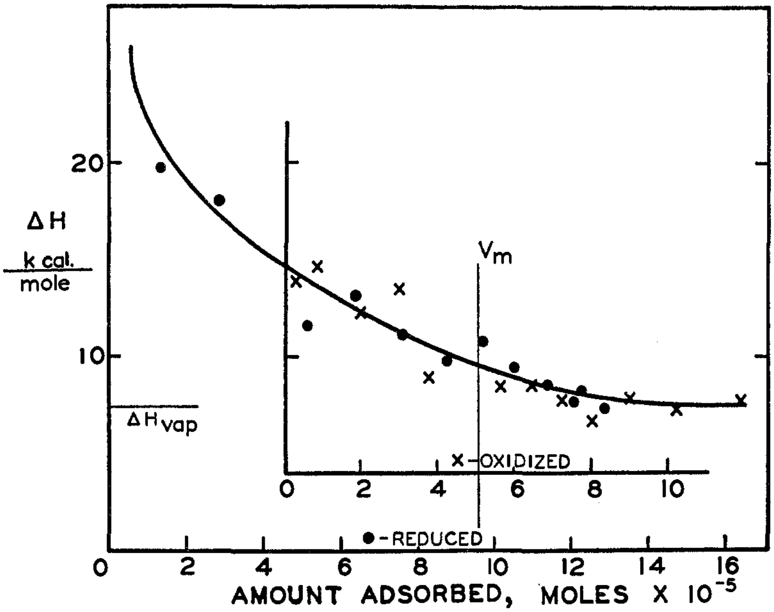

FIG. 6. Decrease in heat of adsorption with increasing coverage for benzene on reduced and on oxidized nickel powder.

greater than that of its ring analog, thiophene. The difference agrees with the known resonance energy of thiophene. The evidence is unmistakable that the stabilizing resonance energy must be paid for during its adsorption. Presumably, as in the case of benzene, the electrons of the ring add to the metal.

It has been mentioned that low heat values are not necessarily an indication of the absence of chemisorption. Furthermore, large changes in work function can accompany physical adsorption, so that a decision cannot always be made on this basis. Inability to remove adsorbed layers by pumping under vacuum at the adsorption temperature is not a clear-cut way to distinguish physical from chemical adsorption; a longer time or lower vacuum might be more effective. It can be shown (99) that if the activation energy for desorption is the same as the heat of adsorption, only 30 per cent may be desorbable at room temperature for a heat of adsorption of about 20 kcal./mole. Well-controlled rate studies of either adsorption or desorption are sparse.

A detailed discussion of the problem for nonmetals developed at a symposium on chemisorption at Keele in 1957 (28).

2. Electronic structure

A concerted effort for many years has been made to connect tendencies toward chemisorption with bulk properties of the metals. Although the surface atom of a material would be expected to be in a quite different state from that of a bulk atom, it is surprising what success has been achieved. For example,

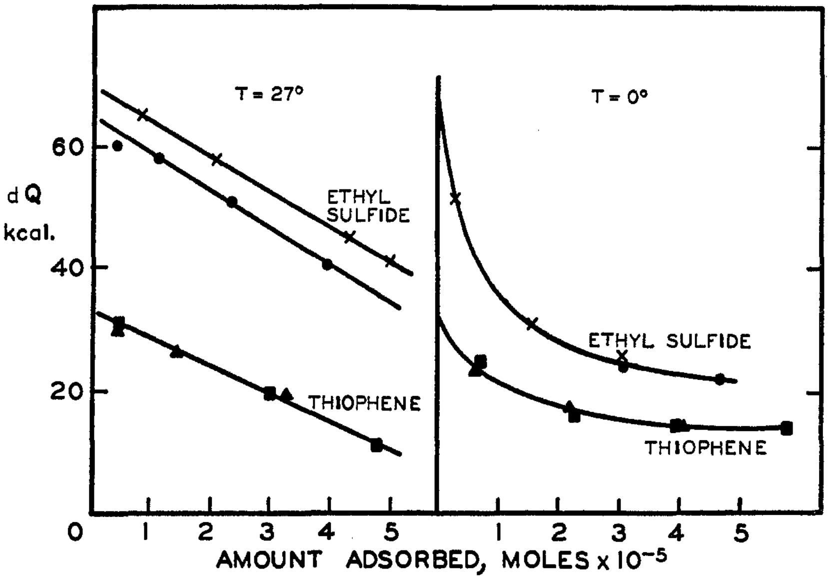

FIG. 7. Heat of adsorption of organic substances on platinum black at two temperatures The difference between the initial values for ethyl sulfide and thiophene is almost exactly the known resonance energy of thiophene. Apparently this energy is adsorbed by the thiophene during the adsorption when the resonance is lost. Adapted from Maxted and Josephs (77); reproduced by permission of the Chemical Society and the authors.

Eley (42) has obtained rather good agreement in some cases between the experimental initial heats of adsorption and those calculated from Pauling's electronegativity scale (87) together with the bond energies between metal atoms and between adsorbate atoms. In addition, the electronic structure of the bulk metals has been emphasized recently.

The *d* metals, those with missing electrons in the *d* band, are generally more active in chemisorption and catalysis than the electron-rich metals, the so-called *s*, *p* metals. A good illustration is provided by the work of Dowden and Reynolds (34) on the hydrogenation of styrene over nickel–copper and nickel–iron alloys. Figure 8 shows that pure nickel is more active in taking up hydrogen than the alloys. The decrease in activity on adding copper can be ascribed to the filling of the *d* band with electrons from the electron-rich copper. In some recent work by Hall and Emmett (52) on the hydrogenation of benzene, zero activity was reached precisely where the *d* band became filled at 40 atomic per cent copper. To put it simply, when the *d* band is filled, the hydrogen cannot become chemisorbed by adding its electron to an unfilled shell. On the other hand, the hydrogenation of ethylene (52) appears to be more complicated.

The reason for the sharp decrease in activity as electron-poor iron is added to nickel is more obscure. The cause is ascribed to the decrease in the number of energy levels, $g(E)$, near the top of the Fermi sea. This quantity arises in the entropy term in the following equation for the ratio of the concentration of ionized to that for the unionized adsorbates:

$$\frac{C_{A^+}}{C_A} = \frac{f(A^+)}{f(A)} \exp.[-\ (I' + \mu_E^m)/kT] \tag{13}$$

where $I' = I + \Delta U^+ =$ ionization potential of adsorbate and adsorption energy of ion,

$f(A^+), f(A) =$ partition functions, and

$$\mu_E^m = -\phi - \frac{\pi^2}{6} k^2\, T^2 \left(\frac{\mathrm{d} \ln N(E)}{\mathrm{d}E}\right)_{E\,=\,-\phi}$$

where $\mu_E^m =$ thermodynamic potential for the metal electron per unit volume,
$\phi =$ electron exit work function,
$T =$ absolute temperature, and
$N(E) =$ number of energy levels between E and $E + \mathrm{d}E$.

Trapnell (105) rated a series of metals for their tendency to chemisorb a variety of gases, and found a good correlation between the *initial* heats of adsorption and the *d*-band character of the metals. Figure 9 shows the plot for the adsorption of ethylene (11). Similar plots have been developed for oxygen, for hydrogen, and for ethylene; as a matter of fact, all of the results can be normalized to the values for one of the metals and most of the points will fall on the same curve.

Beyond the fact that the points for a few metals do not fall on such a curve, the correlation may be questionable. That the explanation of activity on the

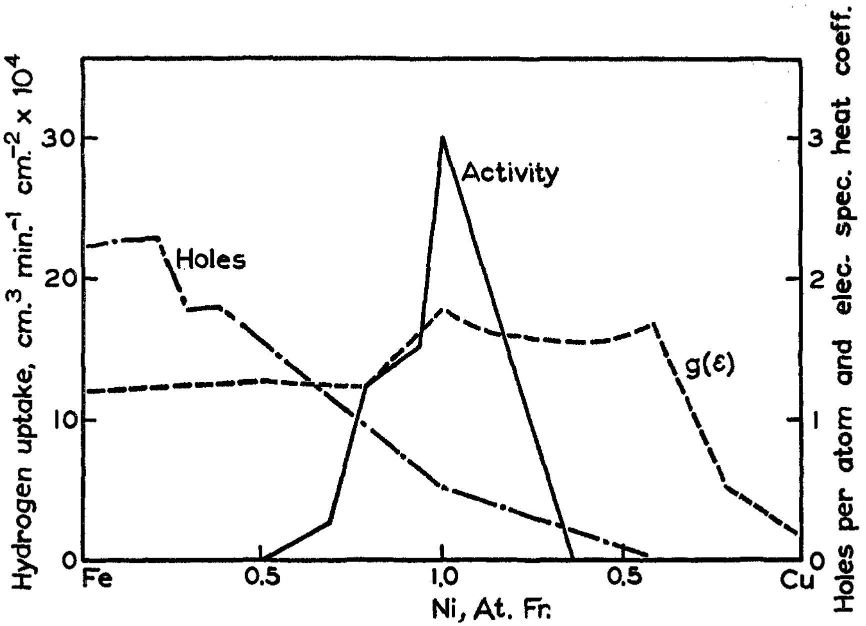

FIG. 8. Hydrogenation of styrene over nickel alloyed with iron and with copper. Adapted from Dowden and Reynolds (34); reproduced by permission of the Faraday Society and the authors.

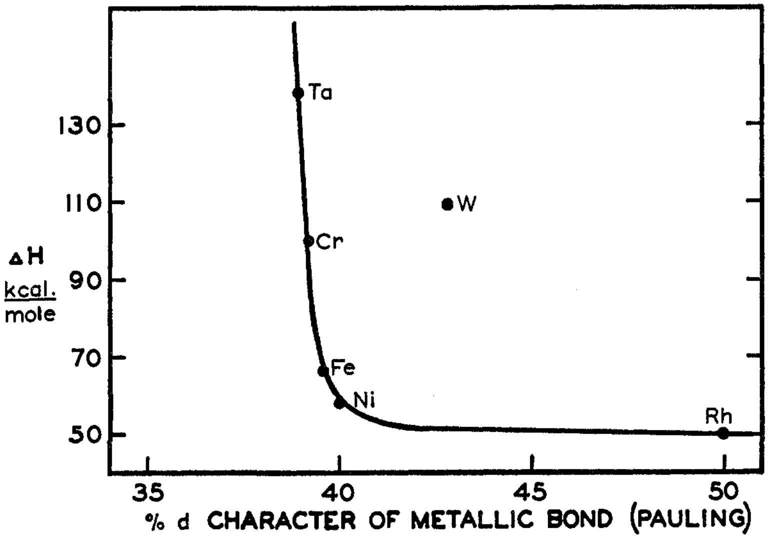

FIG. 9. Heats of adsorption for the first molecules of ethylene adsorbed vs. the *d*-band character of the metals. Adapted from Beeck (11); reproduced by permission of the Faraday Society.

basis of *d* character of bulk metals is not conclusive is demonstrated by the lack of correlation of *d* character with number of unpaired electrons. These would be expected to take part in any chemical interaction with the adsorbate. Also, the rapid decrease in heat of adsorption with very small changes in per cent of *d* character is surprising. Rhodium has a high activity in hydrogenation compared to other metals with similar heats of adsorption; for high catalytic activity, it should be recalled, low heat of adsorption should be preferred, else the binding would be too tight to allow continued reactivity. Numerous attempts have been made to modify the *d* character plots to bring all the points on a line, but the approaches taken are not convincing.

Ferromagnetic alignment is another factor, as suggested by the work of Trapnell (106). Available surface areas of metals before and after chemisorption of simple hydrocarbons were estimated by chemisorption of hydrogen or oxygen. The ferromagnetic metals, iron, cobalt, and nickel, stood apart from other metals because the amount of organic substance adsorbed was almost immeasurable. Their low activity may be ascribed to the ferromagnetic alignment of their unpaired electrons. Presumably energy must be supplied, energy unavailable during adsorption, to activate them for chemisorption.

3. Magnetic susceptibility

Since magnetic susceptibility is a function of the electronic structure of the metal, adsorption which changes the electronic structure of a metal will affect its magnetic properties. For example, supported nickel chemisorbs ethane, as was shown by Selwood's measurements on the change in magnetic susceptibility with coverage (97). Nickel in this form is active. Moreover, the ethane is more effective in lowering magnetic susceptibility with less adsorbed than is the smaller molecule ethylene. This interesting point deserves further examination.

Trapnell (104) reported that one ethylene molecule takes up slightly less than four tungsten sites. Since about 18 per cent of the surface does not chemisorb ethylene, the ratio of 1:4 is almost exact. The ratio might be expected to be 1:2 if the two ethylene carbon atoms with the much smaller hydrogen atoms attach themselves to two tungsten atoms. If hydrogen splits off to occupy two additional tungsten atoms or if the unsaturated carbon atoms each interact with two tungsten atoms, then the ratio of 1:4 can be explained. Infrared spectroscopy will be shown to shed further light on this problem.

The loss in magnetic susceptibility of supported nickel upon the adsorption of hydrogen, benzene, and cyclohexane, as demonstrated by Selwood in figure 10, supports the concept of hydrogen splitting off. The initial rate of fall with coverage for these three adsorbates is approximately 2:6:8. This relationship is to be expected if the hydrogen molecule splits to become chemisorbed as atoms and if one hydrogen splits off from each of the four carbon atoms in cyclohexane which contact the surface in the "boat" form; no hydrogen splits off from the planar benzene ring, in which case six contacts are made.

4. *Electrical resistance*

A decision on electron transfer to or from the metal can often be provided by an increase or decrease, respectively, in electrical resistance. The thickness of the evaporated metal film must not be more than one hundred times that of

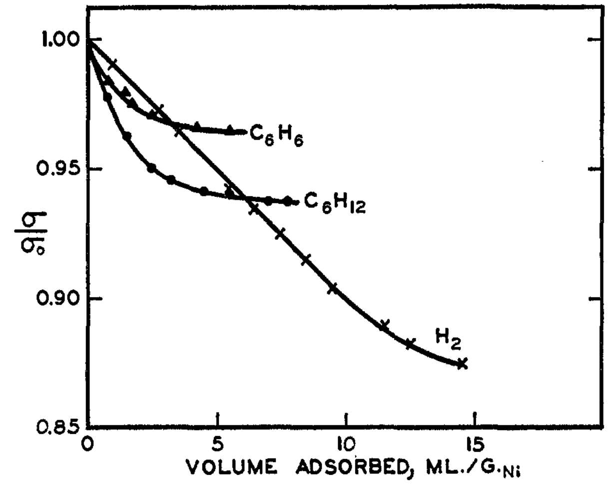

FIG. 10. Magnetization–volume isotherms for nickel kieselguhr at 25°C. The initial rates of loss of magnetic susceptibility of nickel are in the ratio H_2:C_6H_6:C_6H_{12} = 2:6:8. These ratios agree with the concept that the hydrogen is adsorbed as two atoms, the benzene flat takes up six sites, and cyclohexane in the boat form takes up eight sites as four hydrogen atoms split off at the four positions where carbon atoms contact the surface. Adapted from Selwood (97); reproduced by permission of the American Chemical Society.

the adsorbed film for most effective measurements. Changes in contact potential, in magnetic susceptibilities, and in photoelectric effects, on the other hand, are not decisive as far as the complete transfer of electrons is concerned. It will be shown that field emission microscopy does not help very much in this regard, whereas infrared spectroscopy does.

No doubt quite a number of chemical interactions are of the covalent and dative bond types. In these cases, electronegativity shifts occur which are due either to electrostatically induced polarization or to charge transfer of the Mulliken type. It is instructive in this regard to examine the measurement of the electrical resistance of nickel films made by Suhrmann (102). In figure 11 it is seen that when naphthalene or benzene is added the resistance drops. The conclusion is that the π electrons of the ring actually transfer to the metal to cause the lowering of the resistance.

D. EXAMPLES OF TECHNOLOGICAL APPLICATIONS

As was mentioned in the Introduction, surface chemistry encompasses numerous technological applications. Its most important role is to try to provide an understanding of the fundamental nature of the surface interactions involved. Two areas will be discussed here: the mechanism of oxidation, and the growing impact of surface chemistry on the life sciences.

1. *Mechanism of oxidation*

The process by which metals interact with oxygen is one of the most important problems of surface chemistry from a practical standpoint. Indeed, the stagger

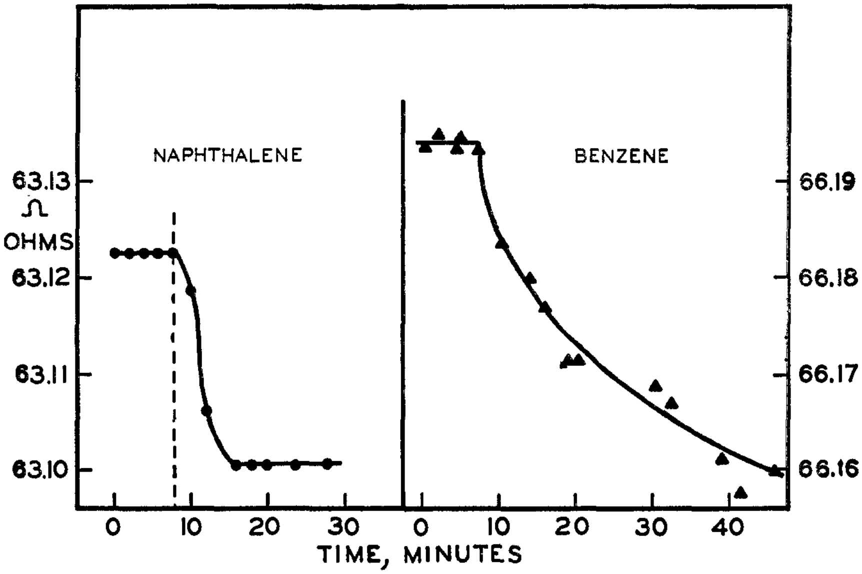

FIG. 11. Decrease in the resistance of nickel films with adsorption of aromatic molecules at 90°K. Adapted from Suhrmann and Schulz (102); reproduced by permission of the Academic Press, Inc.

ing cost in the United States from losses due to corrosion is estimated at six billion dollars per year. The unfortunate aspect of this loss is that too little is yet understood about the mechanism and control of the attack.

Well-established calorimetric measurements have been responsible for much that is known about the reaction between oxygen and metals. For example, measurements of the heat of adsorption on polycrystalline nickel powder (29) confirmed the fact that, after the initial formation of a thin film of nickel oxide, the process continues with the adsorption of O^- ions, as shown in figure 12. The high initial heats are due to the polycrystalline type of heterogeneity mentioned previously. The values at the two plateaus agree with the expected heats of formation of NiO and of O^-, respectively. Thereafter, oxidation is too slow for the calorimeter to follow.

Heat treatment of the freshly oxidized surface changes the O^- layer to an NiO layer by drawing cations through the defect oxide covering. Then the oxidation is rapid again and the heat is near the heat of formation of NiO; a rapid fall to the O^- value is followed by a curious rise toward the end of the fast process. This rise toward the NiO value is presumably due to the field-creating O^- ions pulling nickel ions through the oxide film. An indication of a similar effect was found for molybdenum but not for copper, where it is established by other techniques that the number of field-creating ions is less. There is also the possibility that the initial high heat of adsorption after thermal regeneration is due

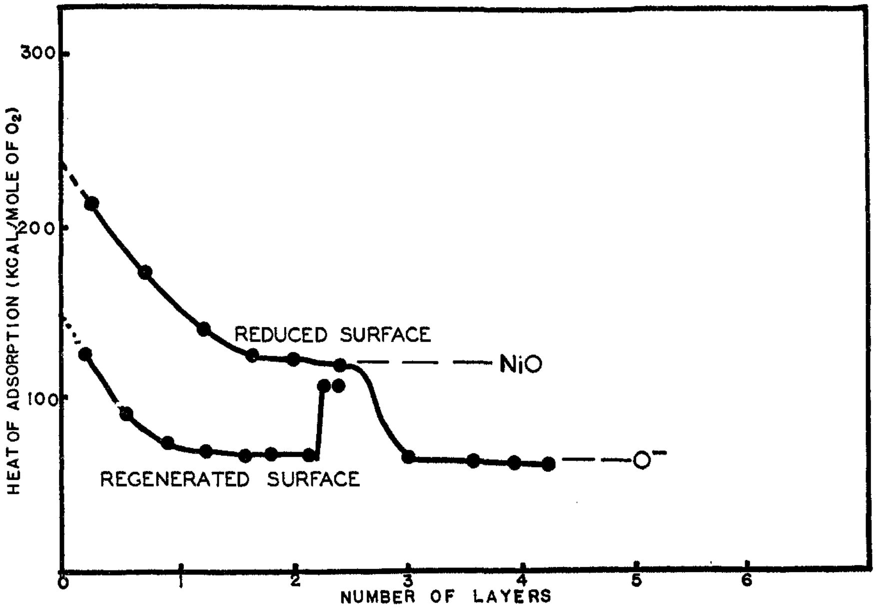

FIG. 12. Calorimetric measurements of heats of adsorption of oxygen on nickel at 25°C. versus coverage. After the reduced surface was first oxidized, the sample was heat treated at 350°C. to produce the regenerated surface on which oxidation was again rapid. From Chessick, Yu, and Zettlemoyer (29).

to the exposure of some bare metal. The controversy over this point needs to be resolved.

One of the methods used to follow O^- ion formation has been changes in the resistance of evaporated metal films as oxygen is added. Another is demonstrated by the direct measurement of the heat of adsorption of water on freshly reduced, freshly oxidized, and regenerated (heat treated) nickel powder as performed in this laboratory (119). The relatively high heat of adsorption on the freshly oxidized surface is due to the strong polarization of the water molecules by the O^- ions. On copper powder, in contrast, such differences were not found.

At −195°C. (liquid-nitrogen temperature), only one layer of oxide forms on nickel (121). On top of this oxide layer is a half-layer of O^- ions (one over each Ni^{++}). Connected with these is a strongly polarized layer of oxygen molecules which can be removed only by pumping at higher temperatures. Overall there is a physically adsorbed layer which is readily pumped off at −195°C. By way of comparison, on molybdenum powder (57) or evaporated film (21) only 10 per cent of the surface is oxidized at −195°C.; it may be regarded that the work function is increased so much that the energy for subsequent removal of electrons is unavailable at −195°C. At this temperature, unsintered molybdenum powder can be oxidized to the extent of 17 per cent; the effect of physical heterogeneities on chemisorption at this low temperature is significant. At higher temperatures physical heterogeneities have much less influence on chemisorption.

A few more words about the status of the understanding of the oxidation of metals seems warranted. The thick-film region where whiskers and other protuberances as well as cracks in the oxide film usually develop form a separate study (see, for example, Gulbranson (51)). In the thin-film region, the pioneering theory of Mott and Cabrera has been found to be inadequate. It is based on the concept of a constant potential across the oxide film as it grows. A constant potential per unit thickness of oxide film does better (116), but the oxidation process is complicated by the presence of defect structures of various kinds, including positive holes, missing ions, etc., as analyzed by Grimley and Trapnell (50) for a variety of combinations. What is needed to decide between the various mechanisms suggested by Grimley and Trapnell is a set of data on adsorption at constant pressure on various metals under a variety of conditions; no one has yet provided these measurements.

2. Interactions with cell membranes

Studies of the interactions of molecules with the surfaces of cell membranes provide an exciting point of juncture for the life scientist and the surface chemist. Recent contributions have an enormous impact, as suggested by the few examples which follow, in the eventual further control of disease and life processes generally.

(a) Attack of red cells

The experiments of Schulman and his coworkers on the attack of cell walls by surface-active agents have been especially valuable. To appreciate the developments, one may examine the molecular anatomy of the red cell membrane in figure 13, looking head-on (85). The phospholipide and protein parts of the membrane are polar and are net negatively charged compared to the less polar and uncharged cholesterol. When either ionic or nonionic surface-active agents attack red cells to destroy them by a process called hemolysis, the question arises as to which part of the surface is disturbed so that the leakage occurs.

Pethica and Schulman (88) tracked down the likely sites of the attack. First they rated the potency of a series of ionic agents in clarifying a given suspension of red cells. Their so-called hemolytic index (h.i.) is the inverse of the potency. Then they studied the effect of the same agents on films of materials such as are present in the cell membranes. These materials (such as lecithin and cholesterol) were spread in turn on water and the resulting films were compressed in a Langmuir balance to a definite pressure. Increasing amounts of each of the ionic agents were injected into the water under the film, and the changes in the film pressures with increasing concentration of surface-active agent were noted. The function that they employed to indicate relative effectiveness of the various agents was the cotangent of the angle of the line produced when the film pressure was plotted against concentration.

For cholesterol films only, an amazingly good correlation was discerned. The inverse hemolytic index, i.e., the potency, forms a smooth curve against the penetration effect on cholesterol films (cot α) in figure 14; at concentrations at which each agent reacts with the film to cause it to reach a pressure of 34 dynes/cm., where it collapses, the agent also causes complete lysis. Cholesterol appears to be the site of the attack by these agents. Moreover, the positively charged agents are not the most potent, as they would be if negatively charged sites were the points of molecular interaction. That is, phosphatide lipides would repel the anionics and attract the cationics.

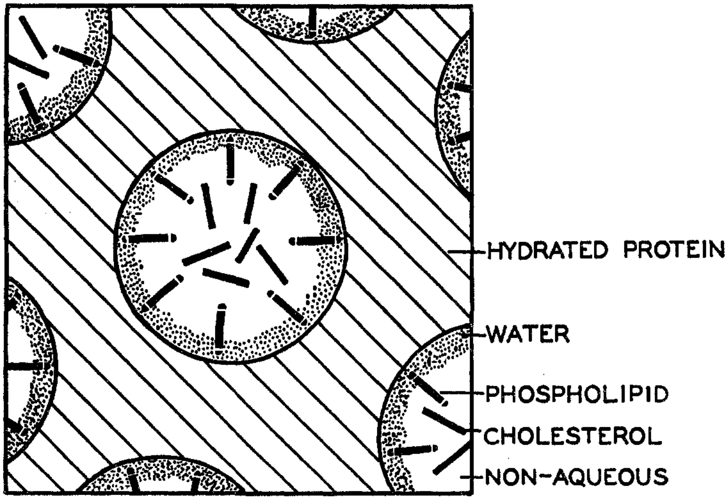

FIG. 13. Anatomy of the red cell membrane. From Parpart and Ballentine (85); reproduced by permission of the Academic Press, Inc.

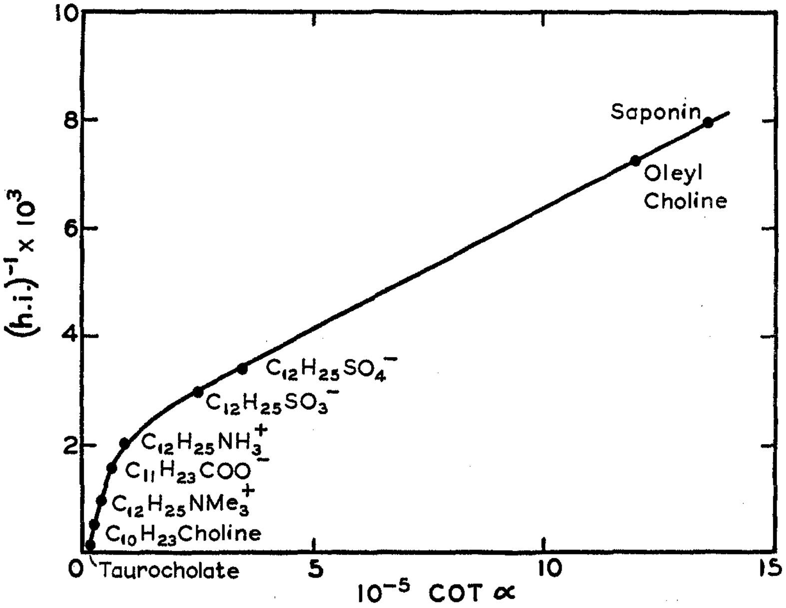

FIG. 14. Potency (inverse of hemolytic index) of ionic agents versus penetration effect on cholesterol films. Adapted from Pethica and Schulman (88); reproduced by permission of the Biochemical Society and the authors.

For nonionic surface-active agents, the situation is quite different. Here, straightforward deterging of the cell wall seems to occur; i.e., lysis occurs at concentrations at which the collapse pressure is reached by the agent alone. For a given agent, the highest potency in hemolysis develops at or near the same concentration at which the lowering of the surface tension of water is greatest. The comparison is given in figure 15 for a polyethylene oxide.

(b) Destruction of bacteria

The corresponding process of destruction of bacteria by leakage of small molecules is also known as lysis. The surface chemistry of the cell walls of bacteria is complicated by the presence of a cheeselike layer; this layer can be removed (109) by enzymolysis, leaving the interior cell wall (called the photoplast membrane) intact and metabolically active in isotonic media. The attack of agents can then be studied without the encumbrance of the outer layer. Only the molecules of the agent which reach the protoplast membrane can be effective in causing destruction by lysis.

The bactericidal action of synthetic detergents has been investigated over the past few years (3, 4, 5, 62) on whole bacteria. In general, anionic detergents are more effective against Gram-positive, whereas cationic detergents have more pronounced action against Gram-negative bacteria. Since the cell walls of the former organisms possess lower lipide content than the latter, it is of considerable interest to learn the precise effectiveness of a series of agents on decapsulated bacteria.

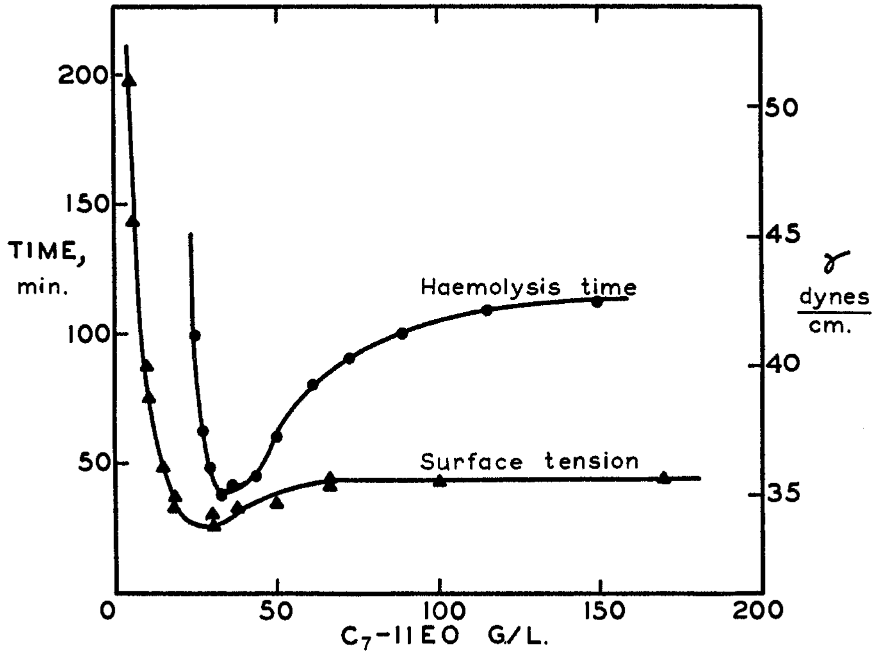

FIG. 15. Haemolytic and surface activity at pH 7 and 20°C. of heptyl alcohol-11-ethylene oxide. From Pethica and Schulman (88); reproduced by permission of the Biochemical Society and the authors.

Gilby and Few (42) pursued the matter for *Micrococcus lysodeikticus.* They showed by infrared analysis that this Gram-negative species has a net negative charge due to a high phospholipide content. The protoplast membrane was much more readily disorganized by the more positive agent in the order:

$$RNH_3^+ > —N(CH_3)_3^+ > —SO_4^- > —SO_3^-$$

The site of attack is quite different here from that in hemolysis. A similar pattern has been developed for the few series of antibiotics that have been studied.

(c) Mechanism of odor

Of man's senses, that of smell has remained most aloof from interpretation on a molecular scale. It is appealing to consider that the primary stimulus is sorptive in character, and support for this sorptive hypothesis has been gained recently. But in the face of a number of other suggested hypotheses, the question had not been entirely resolved.

Moncrieff (80), in a series of experiments with freshly killed sheep's heads, demonstrated that the most potent odorants are more readily taken up by the nostril tissue from gas streams. Davies (33) has contributed significantly by relating the olfactory threshold (lowest concentration at which the odor is detected) to two separate measurable factors: (*1*) the adsorption energies from air to the lipide-aqueous interface of the olfactory membranes; and (*2*) the sizes and shapes of the odorant molecules. The first factor was estimated from measurements of adsorption at oil–water interfaces and from vapor pressures, the second from molecular models. That the shape of a molecule is of some consequence was well known; for example, the olfactory threshold of isopropyl alcohol is one-tenth that of *n*-propyl alcohol. It should also be mentioned that Davies noted a fairly good agreement between hemolytic activity and olfactory threshold; the sorptive viewpoint for both phenomena is thereby strengthened.

From other work it has gradually become clear that an olfactory site is about 65 A.^{2} in area and that there are about 44,000 sites on each nerve cell. Davies considers that the more effective the odorant, the lower is the number of molecules required on a site to cause a "dislocation" resulting in an impulse sent to the brain. (Probably a semiconductor mechanism operates in this step.) When the inverse of the number of molecules, p, required for excitation of a site was plotted versus the cross-sectional area of a large number of odorants, as in figure 16, a surprisingly good correlation was obtained.

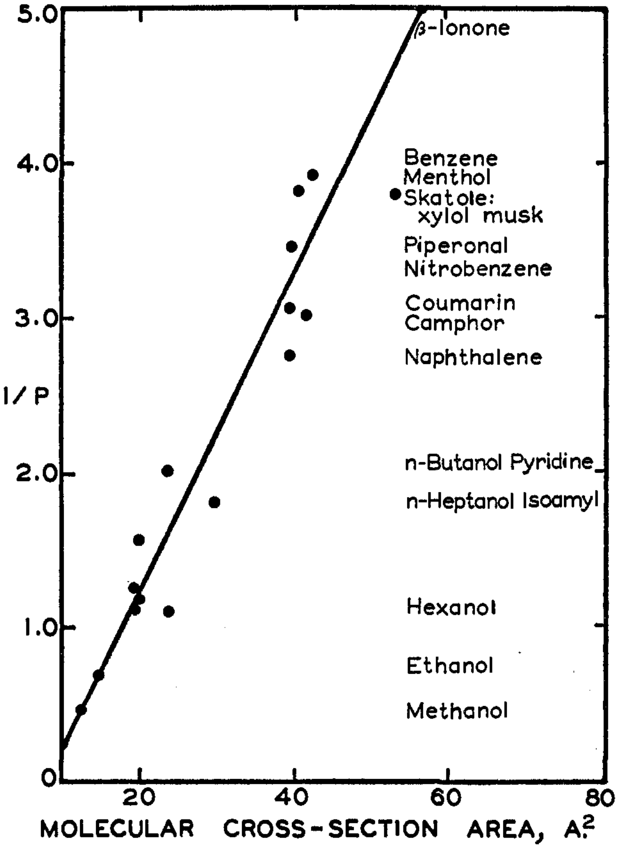

FIG. 16. Inverse of number of molecules required for excitation versus molecular cross-sectional areas of odorants. From Davies (33); reproduced by permission of the Elsevier Publishing Company and the author.

These few examples should serve to indicate that surface chemistry and the life sciences have irrevocably joined forces.

III. New Tools for the Surface Chemist

A. FIELD EMISSION MICROSCOPY

Understanding of the interaction of molecules with metal surfaces in particular has been greatly advanced in recent years by field emission microscopy. Although the behavior of simple systems has been emphasized thus far, no doubt these findings will eventually prove useful for more complex systems.

The field emission microscope was invented in 1936 in Germany by E. W. Mueller (now at Pennsylvania State University), but did not receive general attention until recent years; summaries of previous work have been presented by Becker (9), Gomer (45), and Mueller (81).

1. Principles of operation

In field emission microscopy, the cold emission of electrons from a sharp tip of a wire is portrayed on a fluorescent screen adjacent to a spherical metal anode. A schematic diagram of the field emission microscope is given in figure 17. The wire tip is made sharp by chemical etching so that its radius is of the order of several microns or less.

Electrons are pulled out of the tip by the applied voltage and travel radially in approximately straight lines until they reach the screen, where they activate the phosphor. Here, in magnification of perhaps a millionfold given roughly by the distance to the screen divided by the radius, x/r, the current i of electrons emanating from a small area possessing a uniform work function is given by the Fowler–Nordheim equation:

$$i = AF^2e^{-B\phi^{3/2}/F} \tag{14}$$

where i = current,
A, B = constants,
ϕ = work function, and
F = field strength.

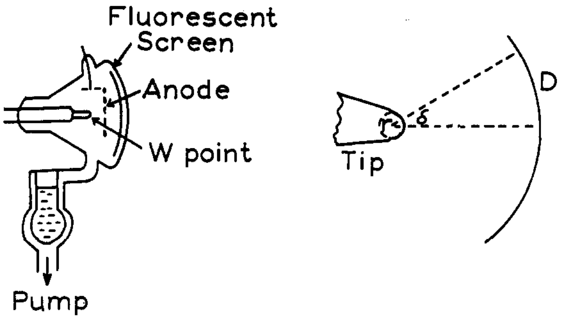

FIG. 17. Field emission microscope

The field strength F, usually of the order of 10^7–10^8 volts/cm., is proportional to the applied voltage; A and B are approximately constant but vary slightly with F and with the work function ϕ.

The wire tip must be heated electrically at pressures of 10^{-8} to 10^{-11} mm. of mercury to get and maintain a clean surface. Under these circumstances, the metal tip must be rather refractory; otherwise it will grow too large by sintering as the impurities are flashed off. The low area of the tip precludes pressures found in ordinary high vacua of 10^{-5} to 10^{-6} mm. of mercury and requires that the entire system up to and including one liquid-nitrogen trap be baked out before proceeding. Without the corollary development of ultra-high-vacuum techniques, the tip would become contaminated before studies could be made.

It should be mentioned here that experiments with hydrogen in the field emission microscope have emphasized the importance of traces of water vapor. For example, if the water pressure is as low as 10^{-9} mm. of mercury when the hydrogen pressure is 10^{-7} mm., the adsorbed water will vitiate any results. As mentioned previously, the effect of trace water is a cause of many problems in surface chemistry studies.

2. Typical patterns

Most of the work reported has been performed on tungsten tips usually flashed to 2400°K. (two-thirds of its melting point) in ultra high vacuum. The surface

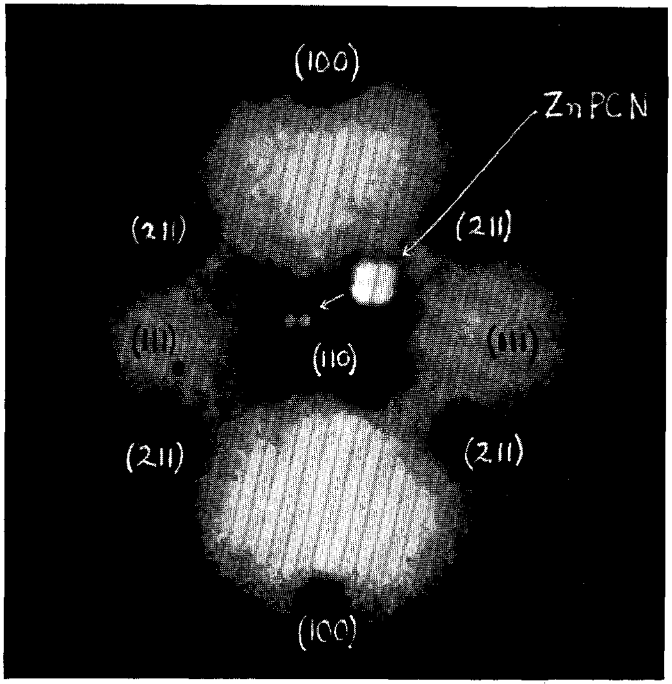

FIG. 18. Field emission microscope pattern produced by a tungsten tip. Reproduced by permission of R. Gomer.

of the resulting tip is so small that it is made of planes of a single crystal (body-centered cubic for tungsten). Figure 18 shows a typical field emission microscope pattern produced by such a tungsten tip. The brightest regions here represent steps, or vicinals, between the (100) and (110) planes. The darkest region is the (110) plane, and the two neighboring bright spots are the (111) planes. It is of philosophical interest that the best evidence for the interpretation of figure 18 is that similar patterns have been obtained in many laboratories.

The brightness of the various regions indicates the ease with which electrons escape from the corresponding planes. The greater the difficulty of removing electrons, the greater is the so-called work function. The (110) plane, to put the results in another way, has the highest packing density and the largest work function, 5.53 electron volts, so the electrons escape from this plane with the greatest difficulty. The (111) plane has the lowest packing density among the planes under discussion, and a work function of 4.39 electron volts. Incidentally, the specific surface energies of the various planes bear an inverse linear relation to the work functions (100). These work functions can be established from log i/F^2 versus $1/F$ plots for the different regions or planes.

3. Location of adsorbed atoms

Field emission microscopy is a particularly potent tool for deciding on what planes adsorption is strongest and for determining the degree of interaction on each plane. In figure 18, for example, two molecules of zinc phthalocyanine or their residues are evident; one appears to be on edge in the (110) plane and the other flat near the corner of this plane. Where the molecules have been sublimed onto the tip, they enhance the liberation of electrons.

Many studies have been conducted with the atomic vapors of electropositive metals like barium fed to the tip. At room temperature, essentially all the atoms which strike the surface stick to it. The decrease in work function confirms the formation of positive ions, since the field of the ions helps to liberate the electrons. The emission pattern reverses itself, because the decrease in work function is greatest for the most dense planes, as might be expected because interaction with the surface is greatest there.

More complicated effects occur when the tip is exposed to molecules like those of oxygen, nitrogen, hydrogen, and methane. For all these, the chemisorbed species form negative dipoles outward which increase the work function and hence the difficulty in liberating electrons. Only a fraction of these molecules which strike the tip are chemisorbed at ordinary temperatures and the remainder evaporate rapidly.

Experiments performed with hydrogen atoms have been especially interesting. Even though hydrogen is sometimes electropositive compared to the metals studied, such as on tungsten, it often decreases the emission and increases the work function. A simple explanation is that the hydrogen ion is so small that it can sink below the electronic plane of the metal so that the dipole layer has its negative side outward. On other metals, such as on nickel, recent evidence (96) is that hydrogen is electronegative even though the bonding is promoted by holes in the *d* band.

4. *Mobility of adsorbed atoms*

Since field emission spectroscopy can show the location of adsorbed species, obviously it can also show when they leave their positions. On raising the temperature, the atoms or molecules become only loosely bonded and can migrate. The movement can be followed by the changes in emission which occur.

The mobility of barium atoms has been followed in this manner. If about one-fifth of a monolayer of barium (1Ba:5W) is adsorbed and the temperature is raised to about 500°K., a bright ellipse develops in the (110) area, showing that the foreign atoms migrate equally well in all directions on this plane. Two bright crescents appear on opposite sides of the (211) plane, showing that they also migrate over this plane, but down the furrows normal to the (111) direction. As the temperature is raised above 500°K., the larger crescents and ellipses increase at the expense of the smaller ones, showing that migration can occur to the edges of lower planes which are closer together so that neighboring edges can cooperate in holding the barium atoms.

The hydrogen mobility experiments of Gomer, Wortmen, and Lundy (48, 111) are especially interesting. The field emission microscope assembly was cooled to temperatures of liquid helium. At such low temperatures high vacua are readily achieved and the sticking coefficient is essentially 1 on all surfaces so that only the area of the tip exposed to the hydrogen stream, fed from zirconium hydride, for example, is at first contaminated.

Below 20°K. type 1 spreading occurs with a sharp boundary like waves of an attacking army being killed off as they attempt to cross a moat. Little or no activation energy is required for the migration. The boundary formed in this way remains stationary below 180°K. unless more hydrogen is added; it is estimated that about 75 per cent of a chemisorbed layer can form below 20°K. without an activation energy. Between 180° and 240°K. a nonuniform boundary diffusion occurs (within a time which is reasonable to follow), fastest along the (110)–(211) zone and slowest along the (110)–(111) zone, but both obeying a distance versus $t^{1/2}$ law, common to surface diffusion. The progressive spreading finally reaches a point where the regions surrounding the (111) and (100) planes have become islands before they are finally flooded.

The temperature dependency of type 2 spreading led to an activation energy of about 6 kcal. along both directions. The spreading occurs here over the smooth close-packed regions, followed by chemisorption in trap sites on the rough regions or steps. At coverages too low for boundary spreading, type 3 spreading occurs at 260–320°K., with various activation energies increasing to 16 kcal. and possibly higher at coverages too low to follow.

A quite similar pattern of results emerges from studies of the mobility of oxygen over a tungsten tip (46). For oxygen, the field emission microscope assembly was cooled to temperatures of liquid hydrogen.

The implications of such studies to the fundamental understanding of both physical and chemical adsorption are obvious, but other fields such as catalysis are enlightened too. To mention one example, catalytic hydrogenation very likely proceeds via mobile hydrogen atoms, rather than some other mechanism, since the measured activation energy for the hydrogenation of ethylene on tungsten at 180°K. is 5–6 kcal.; this magnitude is in accord with the value for the surface migration of hydrogen atoms at a similar temperature, as mentioned above.

Careful work on individual planes is now being done by blocking off all but one area on the screen and then using a photomultiplier tube to measure changes in emission as changes develop on the tip. Such studies at 10^{-2} mm. pressure, for example, show that the strongest bonds are made at coverages up to 1H:1W. The hydrogen molecules are adsorbed strongly in the first layer and weakly in succeeding layers. The sticking probability is about 0.2 (one out of five arrivals sticks) for the atoms in the "first layer," and only about 10^{-2} to 10^{-5} for the second and third layers. As the field is increased in a field emission microscope, the molecules of hydrogen near the tip become polarized so that their arrival rate and sticking probability increase. Above 125 Mv./cm. some of the molecules are so strongly polarized over the most protruding tungsten atoms that they become an ion (H_2^+, and some H^+) and leave the tip; finally, above 200 Mv./cm. only H^+ ions are present to be desorbed. These ions ionize other gas molecules and the total current is thereby increased. Field desorption studies shed light on the polarization of molecules by surfaces. Organic molecules and water vapor (8, 59) give interesting ions even below 10,000 volts/cm. Methyl alcohol yields CH_3O^+ ions; ethane yields $C_2H_5^+$ and CH_3^+; water vapor yields primarily $(H_2O)_2^+$, showing that compound molecules can be formed if the surface concentration is sufficiently high.

5. The field ion microscope

Since 1951, in a clever reversal of the field emission microscope, Mueller and his associates (82) have been developing the so-called field ion microscope. The tip is positively charged so that positive ions from hydrogen or helium at a few microns pressure are emitted. Their large mass leads to a resolving power sufficient to reveal individual atoms because they tend to travel to the phosphor screen in straighter lines than do electrons. Thus, protruding tungsten atoms or adsorbed atoms are seen individually. The particular forte of the field ion microscope appears to be in the study of the location and mobility of atoms at very low coverage and potentially in the study of crystal dislocations in the surface. It might be possible in the future to produce screw dislocations *in situ* following the action in the field ion microscope.

B. INFRARED SPECTROSCOPY

Infrared spectroscopy gained its biggest impetus in surface chemistry studies from Eischens and his coworkers (41) at the Texaco Research Center, Beacon, New York, but earlier work was reported in Russia (70, 112).

1. Special requirements for surface chemistry

For infrared spectroscopy of adsorbed molecules on metal substrates two requirements must be satisfied: the metal particles must be below 300 A., so that absorption of the radiation is not excessive, and the support must be small in particle size, say 150–200 A., so that the radiation lost by scattering is small. Usually it is desired that the support be inert to the gases at the operating temperature. Eischens (39) has found that about 9 per cent of reduced nickel on a nonporous silica, for example, provides a satisfactory system. The infrared studies are carried out directly in the same cell in which reduction and treatment with the gas to be adsorbed takes place, as depicted in the schematic diagram of figure 19. A background spectrum is established for each sample before any gas is admitted.

2. Bonding of molecules

One of the uses of infrared spectroscopy is to learn how molecules are bonded to surfaces. For example, consider the similar spectra observed for carbon monoxide on nickel or palladium, as indicated in figure 20. The band at 4.85 μ is attributed to M—C═O by analogy to spectra of known structures; the bands above 5 μ are attributed to bridge structures. The reasoning is as follows. The band at 5.45 μ appears first at low coverages and the 4.85 μ band due to the weaker linear structure appears last. This latter structure apparently only appears at high coverages when neighboring sites for the bridge structure no longer are available. The several bands above 5 μ may indicate surface heterogeneity, but the evidence from infrared spectroscopy for this point must be considered indecisive.

No band has been recorded in most cases for chemisorbed hydrogen, even though the metals are always reduced before the studies begin; it would be expected to appear in the 3–5 μ region if bonded to a single metal atom and in the 5.2–5.7 μ region if bonded to two atoms. Absorption of the incident radiation by the carrier precludes attempts to discover multicenter bonds which would

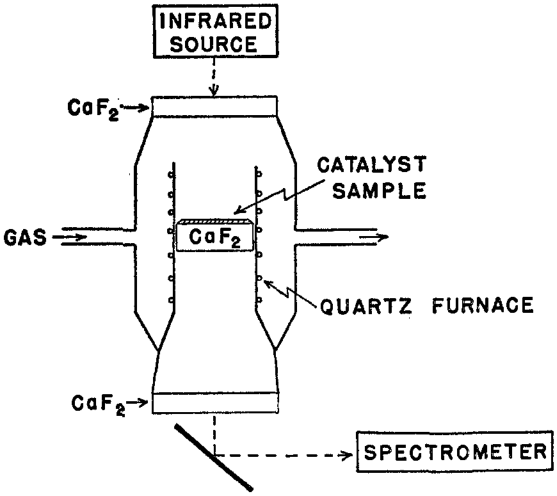

FIG. 19. Cell for infrared study of chemisorbed gases. Adapted from Eischens (39); reproduced by permission of the American Chemical Society.

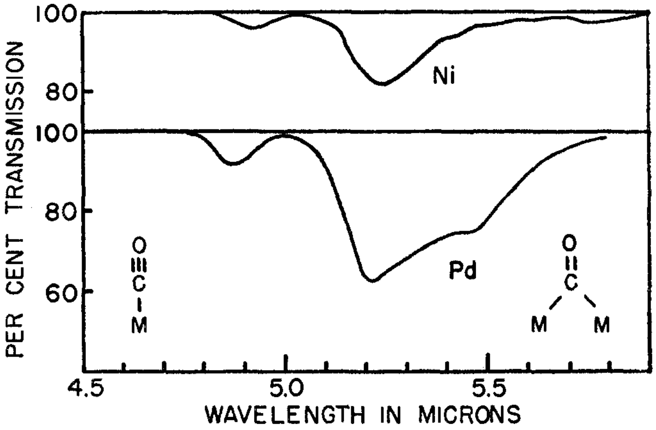

FIG. 20. Spectra for the adsorption of carbon monoxide on nickel and palladium. Reproduced by the courtesy of Eischens and Pliskin.

occur above 7 μ. We have seen that the evidence from field emission microscopy is that at least sometimes the hydrogen is indeed protonic, and the negative evidence from infrared spectroscopy seems to support this contention. Much other controversy in the literature on this point seems now to be resolved. The low-temperature heat-capacity measurements of Aston et al. (2) show that in platinum and palladium the covalent bond does occur; Eischens did detect a band at 4.9 μ after reduction of platinum with hydrogen, a result which he blamed on carbon monoxide impurity.

3. Detection of intermediates

The establishment of bands for intermediates during the course of reactions presents one of the major contributions of the method of infrared spectroscopy. The spectrum for the oxidation of carbon monoxide over nickel at 26°C. is given in figure 21. The process most certainly involves an oxide film on the nickel surface which no doubt forms since the system is not aseptic with regard to oxygen.

The bands at 6.5 and 7.2 μ are ascribed to carbon dioxide, because they persist after the reaction is completed. The band at 4.65 μ is ascribed to the intermediate complex. Eischens (40) attributes this band to an asymmetrical O—C—O vibration in the structure Ni···O—C═O. A second band due to the implied symmetrical vibration is not found; it may be weak or masked by the carbon dioxide bands. It is interesting to speculate on the possible effect of the presence of the field-creating ions O^- established from heat of chemisorption studies as described previously. It would be interesting to compare the same episodes on copper, where the field-creating ions are sparse.

4. Nature of surface interactions

There has long been a question as to whether chemisorption of ethylene on nickel is associative or dissociative in character. Infrared spectroscopy settles the question, but indicates that the answer depends upon the temperature, the heat treatment of the metal surface before use, and the pressure of hydrogen if the hydrogenation process is in progress. There is some question as to what happens on heat treatment, because the solubility of hydrogen in nickel increases with temperature. The freshly reduced and outgassed surface, nevertheless, yields a clear case for associative chemisorption, as shown by figure 22. Bands in the 3.4 μ region are due to C—H stretching in saturated hydrocarbons, and the H—C—H scissors-like deformation band is at 6.91 μ.

Thus, most of the chemisorbed ethylene on this surface is associative, $H_2\overset{\circ}{C}\overset{\circ}{C}H_2$. The small band at 3.3 μ, however, cannot be ignored, since it represents olefinic $\overset{\circ}{C}$—H, which would be fewer in number and characteristically weaker for the same number of molecules adsorbed. Furthermore, at 4 mm. of hydrogen the evidence in figure 23 is that the adsorbed species change to ethyl radicals, CH_2CH_3, and the shoulder at 3.3 μ is eliminated. To put it simply, if the surface is satisfied by addition of hydrogen directly, then the ethylene is not robbed and dissociative adsorption does not occur.

A major contribution of infrared spectroscopy emerges from these remarks. The development of a new band or bands not produced by the bulk material is evidence for a new chemisorbed species. Only on rare and fortuitous occasions would the same bands appear. Physically adsorbed molecules produce only slight shifts from the spectra of the bulk material.

The problems of interactions of molecules with salts, oxides, or organic substances are found to be more complex than those with metals. The presence of positive and negative ion sites and of acid and basic sites on the same surface, plus the more difficult problem of removing small amounts of impurities, which may nevertheless be definitive, must be taken into account. In particular, water in one form or another can dramatically affect the properties of a system through interactions at such interfaces.

Infrared spectroscopy will be used far more widely to solve problems of surface chemistry now that the techniques have been firmly established. And a move

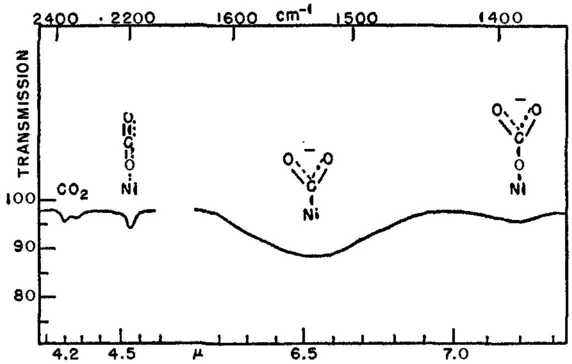

FIG. 21. Spectrum obtained during catalyzed oxidation of carbon monoxide. From Eischens and Pliskin (41); reproduced by permission of Academic Press, Inc.

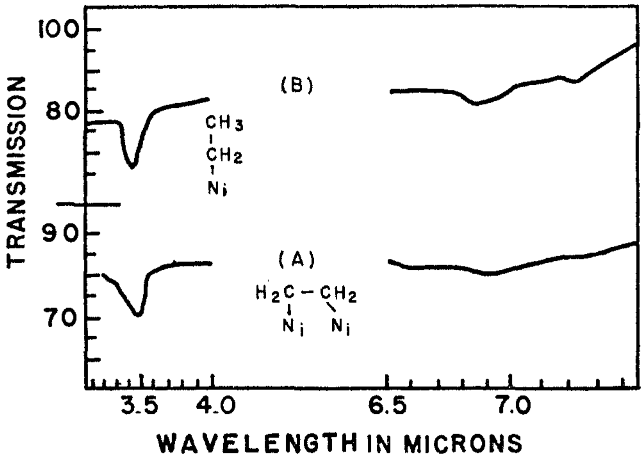

FIG. 22. A, spectrum of ethylene chemisorbed on hydrogen-covered nickel; B, after treatment with hydrogen. From Eischens and Pliskin (41); reproduced by permission of Academic Press, Inc.

toward the study of important problems concerning dielectric surfaces is now under way.

C. HEATS OF IMMERSION

Heats of immersion techniques appear to be particularly fruitful for the study of interactions with dielectric solids of high area. The first impetus was given to such studies by Harkins (26, 54, 55), starting about 1930.

1. *Thermistor calorimeters*

The heats of immersion technique has recently gained renewed attention, owing to the development of simple thermistor calorimeters (120). The simple calorimeter diagrammed in figure 23 will suffice to measure heats of immersion of polar surfaces if the area of the sample exceeds 10–20 sq. m. per gram. The heat of immersion for each unit area of surface, h_i, corrected for the enthalpy of the liquid surface, h_L, is the net integral energy of adsorption. This quantity is the number of moles adsorbed per square centimeter multiplied by Avogadro's number and by the differences between the energy of a molecule in the adsorbed and the liquid states. The net integral energy of adsorption is, in turn, for a group of similar peripheral dipole molecules, equal to their energy of interaction with a molar surface:

$$h_i - h_L = n(e_A - e_L)N = E_\mu = F\mu$$

Heats of immersion are now serving several purposes: to rate the average polarity of the surface, to rate hydrophilicity, to estimate the site-energy distribution for a given adsorbate, and to rate the wetting tendency of a number of surfactants for a hydrophobic surface. Other uses which are gaining impetus are in the studies of surface heterogeneities and solution adsorption.

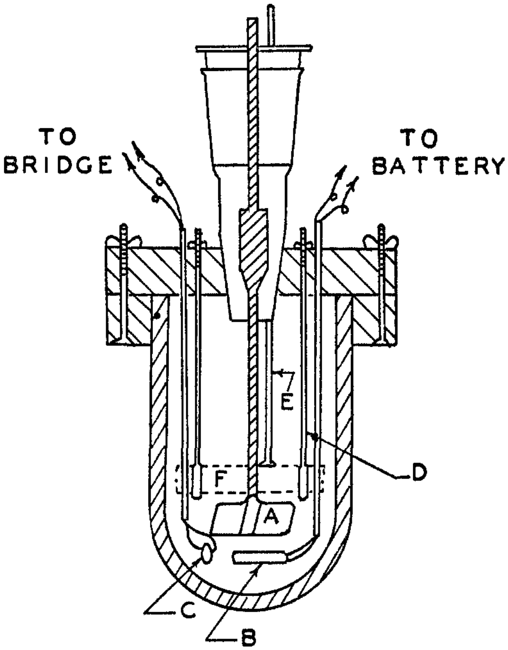

FIG. 23. Heat of immersion calorimeter. From Zettlemoyer, Young, Chessick, and Healey (120); reproduced by permission of the American Chemical Society.

2. Average polarity of solids

The concept of rating the polarity of solids first arose from the observation that the heat of wetting of rutile in various butyl derivatives increased linearly with the dipole moment of the derivative (58). From the slope of the line shown in figure 24 (32), the average polarity F of rutile is calculated to be 2.7×10^5 e.s.u. Important assumptions are that the butyl derivatives used as immersion liquids have about the same cross-sectional areas, that distances from dipoles to the surface are roughly the same for each molecule, and that the interactions with neighboring molecules are the same whether adsorbed or in the bulk liquid.

The average electrostatic fields of a number of solids are rated in figure 25 (118). The calcium fluoride was chosen for comparison with rutile because its negative ion is less polarizable than the positive ion, whereas usually the opposite is true in rutile. The more polarizable ion can adapt itself to the surface more readily and so is likely to protrude slightly, as mentioned earlier. Aerosil is a partly hydrophobic silica shown by a lower apparent water area than its nitrogen area; thus, the slope of the line for this substance represents an average of widely different surface regions. Graphon, a graphitic carbon black, and Teflon, a polytetrafluoroethylene, possess very small electrostatic fields. Yet the differences between the levels of the horizontal lines show that Teflon has a considerably lower surface energy than Graphon; the interaction for these substances is almost entirely due to nonpolar van der Waals forces. Except for these last hydrophobic surfaces and for the most polar immersion liquids, the absence of

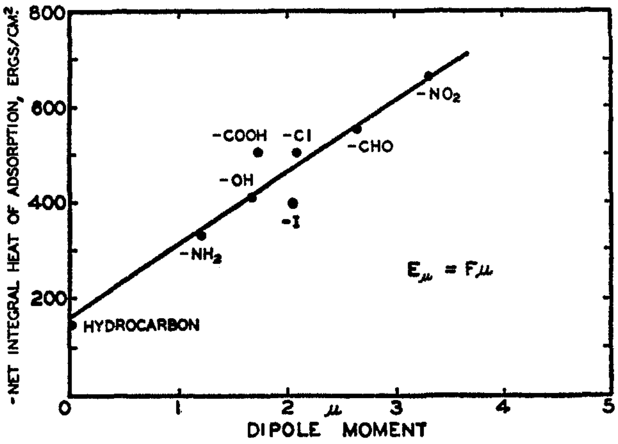

FIG. 24. Net integral heat of adsorption for various butyl derivatives on rutile (TiO_2) as a function of the dipole moment of the liquid. From Chessick, Zettlemoyer, and Healey (32).

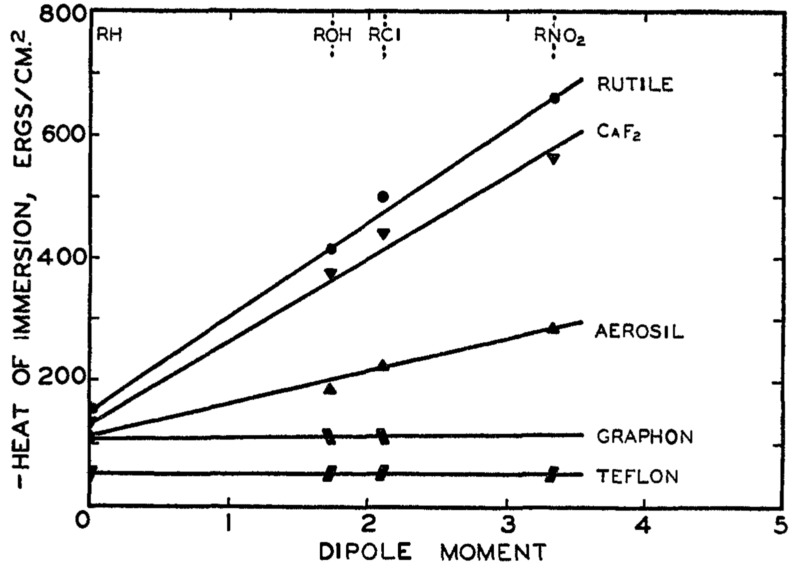

FIG. 25. Heats of immersion of butyl derivatives on various surfaces as a function of the dipole moment of the liquid. From Zettlemoyer, Chessick, and Hollabaugh (118); reproduced by permission of the American Chemical Society.

traces of water is essential to obtain correct (lower) values for heats of immersion.

More heat of immersion work has been done on titanium dioxide, both the rutile and the anatase forms, than on any other solid substrate. In some ways this is unfortunate. While it is the most important synthetic inorganic chemical of commerce, it has not been easily obtained in a pure form in the past and much work has been reported on samples containing sufficient impurities to raise doubt that a surface of titanium dioxide was entirely responsible for the results. In addition, the polycrystallinity of all the samples studied makes this sort of heterogeneity prevalent. Happily, the combination of the two dominant attraction forces—dispersion forces and polarization forces, which are maximum where the other are minimum—tends to reduce the importance of this latter type of heterogeneity. Fortunately, too, the hydroxide of titanium is unknown, so that one would not expect hydroxyl groups to form on the surface. But there is something curious about the surface of titanium dioxide: it chemisorbs alcohols, amines, and the like over a large percentage of its surface. High heats of adsorption and difficulty in removal by pumping are used here as criteria for chemisorption.

3. Hydrophilicity

Hydrophilicity can be evaluated by comparing directly the heat of wetting of various solids in water. This method is useful even if water vapor is adsorbed over the entire sample surface. In the latter case, the difference between nitrogen and water surface areas cannot be used, nor can contact angles, which would be zero for all such cases. The heat of immersion in water always reflects the hydrophilic character of the solid surface as prepared previously. Thus, if the outgassing removed chemisorbed water, for example, converted —OH groups on silica to siloxane groups —Si—O—Si, this will show up in the heat values. For complex surfaces, therefore, a study may have to be made to evaluate such special effects, as the outgassing conditions are varied.

4. Wetting tendency

The effective characterization of the wetting tendency of surface-active agents has been sought after in many fields where they are used. In detergency, for example, the wetting tendency of surfactants for hydrophobic dirts would establish values for one step in the washing process. Measurements of heats of immersion for a graphitic material into surfactant solutions provide an adequate way to rate their wetting tendency, as indicated in table 1. Graphon has a heat of immersion in water of only 32 ergs/cm.^{2}, so that the enhancement caused by the surfactants is considerable. That detergency tests with these surfactants (for those tested) fall in the same order as the heats of immersion may be fortuitous; other factors such as suspension and redeposition of soil are almost as important.

5. Site-energy distribution

Perhaps what will emerge as the most valuable use of heat of immersion techniques is the study of surface heterogeneities. As an example, consider the acid sites on attapulgite (115), an acicular hydrated magnesium silicate. The outgassed attapulgite was first treated to butylamine vapor for several hours at room temperature. When the residual vapor was pumped off, some of the amine remained chemisorbed on the acid sites. That the amine was desorbed gradually

TABLE 1

Heats of immersion of Graphon in 0.50 per cent aqueous solutions of surfactants

Surfactant	Approximate Purity	Heat of Immersion	Type
	per cent	*ergs/cm.*^{2}	
Sodium lauryl sulfate*	100	142	Anionic
Purified sodium dodecylbenzenesulfonate	100	120	Anionic
Sodium dodecylbenzenesulfonate (Santomerse-3)†	99	73	Anionic
Monobutyl biphenyl sodium monosulfonate (Aresket-300)†	—	78	Anionic
Monobutyl phenylphenol sodium monosulfonate (Areskap-100)†	—	51	Anionic
Sodium decylbenzenesulfonate (Santomerse-D)†	90	47	Anionic
Sulfate ester of an alkyl phenoxy polyoxyethylene ethanol (Alipal CO-436)‡	—	68	Anionic
Polyoxyethylated nonylphenols‡			
Igepal CO-650	99	88	Nonionic
Igepal CO-850	99	60	Nonionic
Igepal CO-530	99	40	Nonionic

* Supplied by National Bureau of Standards, Washington, D. C.

† Supplied by Monsanto Chemical Co., St. Louis, Missouri.

‡ Supplied by General Aniline and Film Corporation, Easton, Pennsylvania.

as the temperature was increased indicates a distribution of site strengths. Heats of immersion in liquid butylamine were then determined on successive portions of attapulgite as the amine was removed by desorption at higher and higher temperatures. After degassing at 400°C., the value of the heat of immersion corresponded to that for the original attapulgite.

From these results, the acid site-energy distribution for chemisorption of butylamine could be calculated, as depicted in figure 26. The distribution might be expected to be different for a base of different strength; so a three-dimensional map of site-energy distribution could be developed by using several adsorbates. Extension of these remarks to the case of petroleum-cracking catalysts is obvious. Here the acid sites arise from the substitution of trivalent aluminum for quadrivalent silicon in the silica lattice. The previously mentioned question of whether the acid sites are Lewis or Brønsted in nature is now being resolved by measurements made in the presence and absence of small amounts of water.

6. *Nature of the interface in solution adsorption*

Future important contributions of heats of immersion will be in the field of solution adsorption. When two (or more) components are present in a liquid and when the preference for adsorption of the one component is not preponderant (as for graphite into organic solutions), it is not possible to establish with certainty the practical boundaries of the interfacial region. Therefore, the amounts of the two components adsorbed cannot be decided. Much can be learned, however, by studying the heats of immersion of the solid into two component solutions of varying composition. One rather simple system of butanol and water onto graphite has already been elucidated by this technique (113). The importance to many technologies of understanding solution adsorption cannot be overestimated.

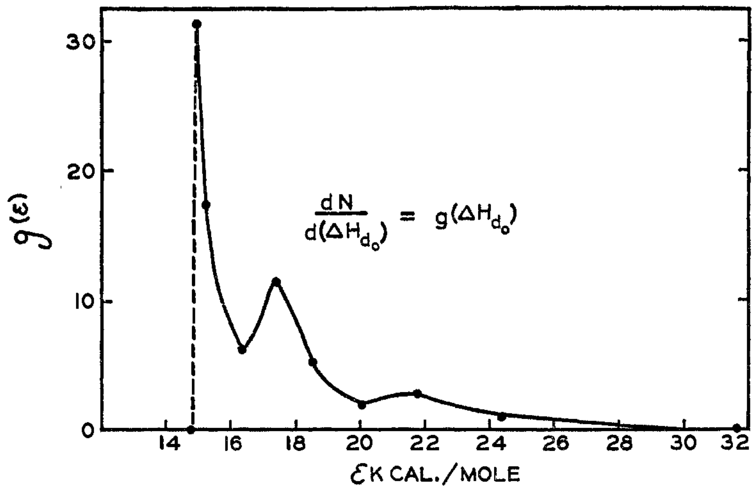

FIG. 26. Distribution of acid sites for butylamine on attapulgite. From Young, Chessick, and Healey (115); reproduced by permission of the American Chemical Society.

D. NUCLEAR MAGNETIC RESONANCE

It appears that data from nuclear magnetic resonance can shed further light on such problems as have been discussed. Bloch (12, 13) and Purcell (90, 91) discovered nuclear magnetic resonance in 1946, and although hundreds of contributions have been published since that time, few have yet to deal with problems of surface chemistry. Since the response of hydrogen is especially high, the use of nuclear magnetic resonance to study surface water, surface hydroxyl groups, and the adsorption of organic molecules appears particularly promising.

1. *Surface water*

An interesting example of its possibilities is provided by the work of Zimmerman and Lasater (122, 123) on the problem of the adsorption of water on silica gel. Figure 27 shows the transverse relaxation times of the protons of the water at various coverages. Above two layers at the right in the diagram, a distinct resolution into two groups of water molecules was obtained. The group corresponding to shorter time (T_2) is in the first layer and more closely associated with the surface; therefore $T_{21} < T_{22}$. The slight increase in T_2 shows that the random motion of the molecules in the first layer is somewhat increased as they become covered with the second layer.

Between two layers and above one-half layer, the results show a single-phase system, so that apparently all the hydrogen nuclei enjoy the same average local interaction. Such a change is often noticed in studies of heats of adsorption at this same coverage, as described earlier for Rhodin's study of the physical adsorption of nitrogen on copper.

The curious finding, however, is the resolution of a second absorbing phase at the low coverages. The small relaxation time associated with this phase shows

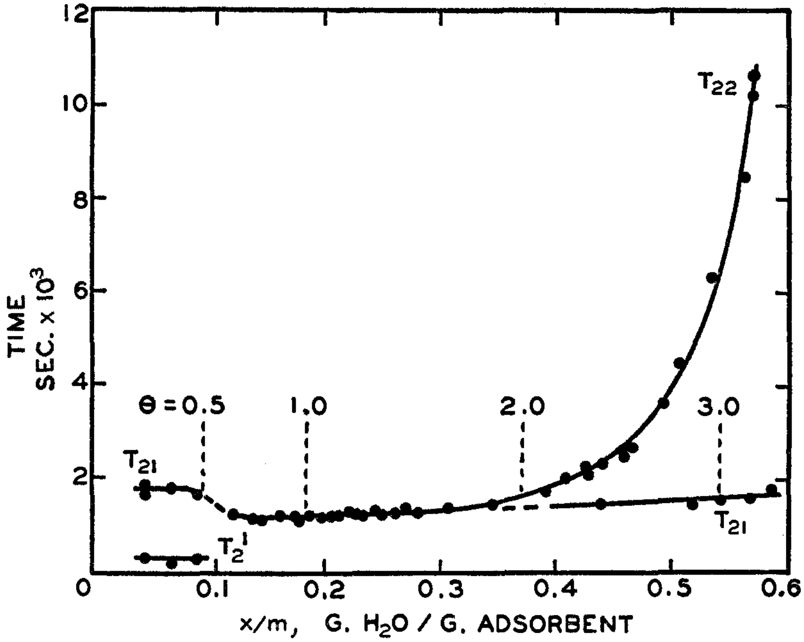

FIG. 27. Transverse relaxation time for water on silica gel. From Zimmerman, Holmes, and Lasater (122); reproduced by permission of the American Chemical Society.

that a few water molecules are bound much more tightly than the others. The sites responsible appear to arise from 0.2 per cent of alumina as an impurity, which perhaps are there as acid sites as in the cracking catalysts mentioned previously, and which adsorb the water more strongly than the bulk silica. The use of nuclear magnetic resonance to extend such studies to the adsorption of alcohols, amines, and hydrocarbons is indicated.

2. Depth of surface forces

The question of the depth into the liquid phase to which the surface forces operate has been attacked by many techniques with quite varying results from 10–200 A. up to 1–2000 A. The frequency shift of the proton resonance of *n*-heptane on carbon blacks has now been used by Graham and Phillips (49) to study the depth of the liquid layer influenced by the solid surface. The magnitude of the observed shift (see figure 28) decreases with increasing film thickness to a plateau, but, owing to effects caused by the adsorbent, the shift does not decrease to zero. It is estimated that the perturbed region has a thickness of about 28 A. or about seven layers. Similar magnitudes were obtained from a number of other adsorbates. The shifts are explained in terms of different amounts of shielding of the paramagnetism of the surface due to unpaired electrons. The conclusions from the nuclear magnetic resonance measurements seem reasonable and are in accord with direct adsorption studies such as those of Harkins (53), who estimated surface layers at five to ten molecules deep.

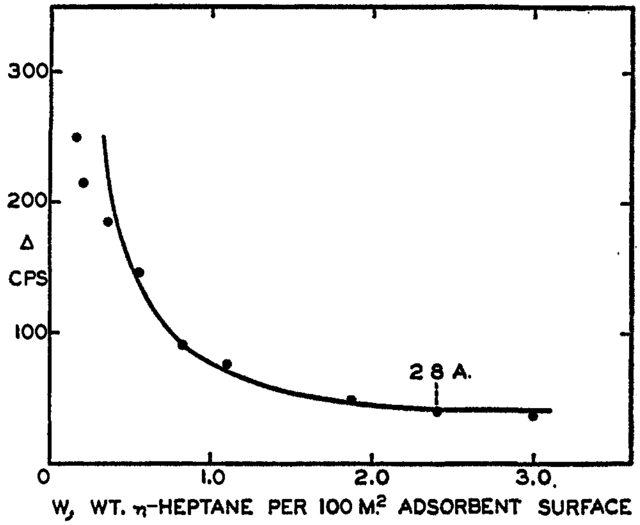

FIG. 28. Shift in nuclear magnetic resonance frequency with coverages for heptane on acetylene black. From Graham and Phillips (49); reproduced by permission of Butterworths Scientific Publications, Ltd.

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