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Surface Science

An old field rejuvenated, demands attention and people.

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Summary. During the past 15 years, surfaces have been increasingly studied on the atomic scale. As a result, their atomic structure and composition and the dynamics of gas-surface interactions are much better understood. Modern surface science is beginning to have an impact on many technologies. Techniques are readily available to study solid-vacuum and solid-gas interfaces. Studies of solid-liquid and solid-solid interfaces are difficult and appear to be challenging frontier areas of research. Surface science is at the heart of most research and development problems in energy conversion and storage.

Systems with a high surface area, A, or surface-to-volume ratio, A/V, have played important roles in evolution and in our lives. The human brain has a large area, almost ten times that of an ape brain, while its volume has increased only sevenfold (*1*). The coral reef, the leaf and other photosynthetic systems, and our bone structure, stomach lining, and skin are all high A/V systems. It appears that an increase of the A/V ratio leads to optimum reaction rates and chemical selectivity. Colloids that are stable high A/V systems play dominant roles in soil chemistry and food processing and in the paper, paint, and rubber industries, just to name a few areas of application. Chemical reactions are catalyzed by surfaces to achieve thermodynamic equilibrium and to be carried out selectively when in competition with other reactions that are thermodynamically equally feasible. This is the role of heterogeneous and enzyme catalysts, which now are basic ingredients of most chemical technologies.

The importance of surfaces has been recognized from the beginning of the development of chemical sciences. Determinations of the surface tension of liquids, the amounts of gases adsorbed in porous solids, or the amounts vaporized were all possible a century ago, and these experimental quantities could be related to surface thermodynamic parameters. Gibbs developed much of the framework of surface thermodynamics that we employ today. Adhesion and friction as well as lubrication were important concerns during the latter part of the 19th century. Progress in surface science was rapid during the first four decades of this century. The synthesis of ammonia over iron that was "promoted" (that is, improved) by additives such as potassium and calcium and the oxidation of ammonia over platinum focused attention on transition metals as catalysts. Hydrogenation of carbon monoxide over ruthenium, nickel, cobalt, iron, and thorium oxide catalyst surfaces became one of the most important sources of gasoline, methane, and other chemicals in Germany and much of Europe before and during World War II. Adsorption and gas-surface interactions became better understood in connection with the development of the light bulb. The properties of surface space charge and electrical double layers at surfaces were discovered and explored in connection with electrochemical processes. The various surface characterization techniques that were developed during this period have provided much information about macroscopic properties of surfaces (surface areas, average heats of adsorption, and rates and activation energies of surface reactions).

During the next stage of development of chemistry, surfaces did not fare well. Researchers in physical chemistry turned toward investigating molecular properties, utilizing the rapidly developing spectroscopic techniques and x-ray diffraction. Then information on molecular structure was related to the dynamics of chemical reactions, which, with the advent of relaxation spectroscopy and molecular beam scattering techniques, could also be scrutinized on the molecular scale. Surface science could not participate in this development, mostly for the following reasons. The volume density of a solid, such as ice, is about $\rho = 3 \times 10^{22}$ molecules per cubic centimeter. The surface concentration is about $(A) = \rho^{2/3} = 10^{15}$ molecules per square centimeter. Defining the surface to be studied as the topmost layer of atoms, one must obtain detectable signals from 10^{15} atoms or molecules in the background of 10^{22} atoms or molecules to obtain surface information. Because of the low scattering cross section of surface molecules, they are not amenable to study by most of the experimental techniques that successfully use electromagnetic radiation to study molecular properties in the gas or in the solid state, unless these techniques are employed in very special configurations and circumstances. In addition, the effort needed to obtain clean or reproducible surfaces is formidable.

During the 1950's marked changes be-

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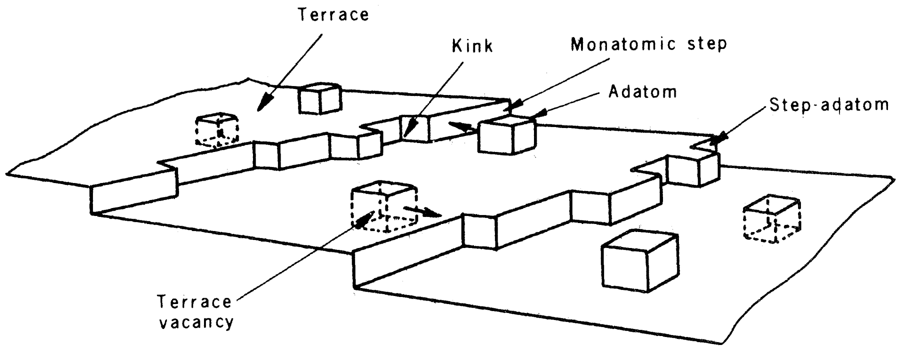

Fig. 1. Schematic representation of the heterogeneous surface on the atomic scale. Terrace, step, and kink atoms as well as point defects (adatoms and vacancies) have been identified by experiments.

gan to take place in surface science. These were largely connected with the development of the electronics and computer industries and with the rise of aerospace technology. Less expensive and faster devices could be fabricated by miniaturization, which meant an ever-increasing A/V ratio. Thus, surface characterizations and the study of the physical chemical properties of the surface layer by and large controlled the rate of development in semiconductor device technology. Space exploration necessitated the development of ultrahigh-vacuum technology (pressures less than 10^{-8} torr), which permitted the preparation of clean surfaces and more reproducible surface studies. There was an explosive development of new techniques that yielded information about the atomic and electronic structure, composition, and oxidation states of all types of surfaces. A partial listing of the techniques that are utilized most frequently is given in Table 1. Surface chemical analysis, which had eluded the chemist for so long, can now be carried out with a sensitivity of less than 1 percent of a monolayer (less than 10^{13} atoms per square centimeter) over an area of much less than 1 square millimeter (10^3 to 10^6 square angstroms). It is no longer necessary to study samples with large surface areas (often more than 10^2 square meters per gram) to obtain detectable surface signals. A 1-cm^2 surface is sufficient for most surface chemical studies.

In the past 10 years there has been an accelerated development of our understanding of surfaces on the atomic scale. Modern surface science has emerged, and its impact on various technologies is beginning to be felt. I will attempt here to review the status of our knowledge of the composition and structure of surfaces, the surface chemical bond, and the dynamics of gas-surface interactions, especially as some of these studies apply to heterogeneous catalysis. Then I will point out the areas of surface science where development is lagging and the possible directions of research for the near future.

Some of the Unique Physical Chemical Properties of Surfaces

The surface of a solid is heterogeneous on the atomic scale. Figure 1 depicts schematically the various surface sites that are identified by experiments. There are atoms in terraces, which are surrounded by the largest number of nearest neighbors. Atoms in steps have fewer nearest neighbors, and atoms at kink sites have even fewer. Kink, step, and terrace atoms have large equilibrium concentrations on any real surface. Point defects such as adatoms (adsorbed atoms) and vacancies are also present and are important participants in atomic transport along the surface, although their equilibrium concentrations are much less than 1 percent of a monolayer, even at the melting point.

Studies of transition metal and oxide surfaces have yielded a great deal of experimental evidence that different types of surface sites have different chemistries (*2–6*). This is exhibited in the large differences between the heats of adsorption of molecules at the various sites (*7*) and in their differing ability to break high-energy chemical bonds (H-H, C-H, N-O, N-N, and C-O bonds) (*8, 9*). These effects have been explained theoretically (*10*) in terms of large variations in the localized charged density distributions as a result of the structural differences (variations in crystal field splitting) and the appearance of large surface dipoles due to redistribution of the charge density of the electron gas at these various sites in metals. Herein lies one of the important reasons for the complexity and the diversity of surface chemistry. The overall rate and product distribution in a surface reaction is the result of rates and products that form at each surface site. From measurements of these macroscopic parameters for reactions over a heterogeneous surface, it is very difficult to identify the elementary chemical processes associated with each site. Moreover, since the preparation of the surface establishes the relative concentration of each site, the chemical properties intimately depend on surface preparation.

The heterogeneous surface is covered with a near monolayer of adsorbate un-

Table 1. Partial listing of techniques most frequently utilized at present for studies of surfaces in a vacuum.

Technique	Atomic process	Main information	Sensitivity (monolayer)	Depth sampled (layers)
Low-energy electron diffraction (LEED)	Elastic backscattering of electrons in the 10- to 200-eV range	Surface structure	$\sim 10^{-2}$ to 10^{-1}	1 to 7
X-ray photoelectron spectroscopy (XPS)	Electron emission from atoms at the surface	Oxidation state, composition	$\sim 10^{-2}$ to 10^{-1}	1 to 7
Auger electron spectroscopy (AES)	Electron emission induced by the deexcitation of atoms; initial excitation by electron or ion impact	Surface composition; qualitative and quantitative	$\sim 10^{-3}$ to 10^{-2}	1 to 7
High-resolution electron loss spectroscopy (HRELS)	Inelastic backscattering of electrons in the 1- to 30-eV range	Vibrational spectrum of adsorbed atoms and molecules	$\sim 10^{-3}$ to 10^{-2}	1
Ion scattering spectroscopy (ISS)	Inelastic backscattering of ions at ~1 keV	Surface composition	$\sim 10^{-3}$ to 10^{-2}	1
Secondary ion mass spectroscopy (SIMS)	Mass analysis of ionized surface atoms ejected by ion impact at ~1 keV	Surface composition	$\sim 10^{-6}$	1

der most experimental conditions. This layer is present when the surface is exposed to the ambient atmosphere or during surface chemical reactions. The adsorbate may impart to the surface unique chemical properties by blocking sites or changing the oxidation states of surface atoms. The presence of adsorbates changes the nature of bonding of incoming reactants, reaction intermediates, and product molecules. Such an adsorbed overlayer is schematically represented in Fig. 2. Not only the chemical but also the mechanical properties of the surface (friction, adhesion, and resistance to mechanical or chemical attack) are affected by the presence of the adsorbate. Manipulating the adsorbed layer by depositing chemically active additives permits a great deal of control of important surface properties such as catalysis or corrosion inhibition. There are several reasons for the formation of an adsorbed monolayer. Molecules approaching the surface experience a net attractive potential that may trap them for a finite residence time. The surface free energy is always positive; thus, the surface would like to be covered by atoms or molecules that would lower the surface free energy. Carbon, hydrocarbons, oxygen, sulfur, and water are among the most common adsorbates on surfaces that are exposed to the ambient conditions of this planet.

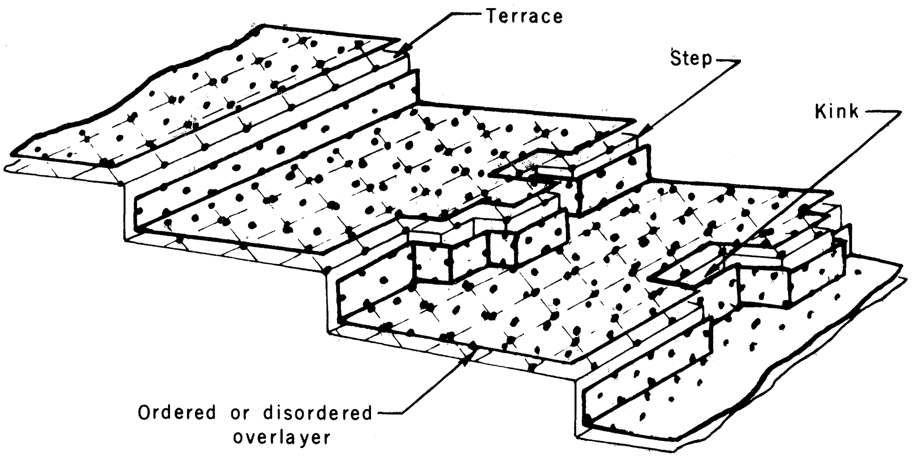

Fig. 2. Schematic representation of the surface when covered with a near monolayer of an adsorbate or a deposit.

The two-dimensional phase approximation. There is a great deal of exchange among atoms and molecules that are adsorbed at the different surface sites. This is because the activation energies for transport along the surface are low compared to the energy needed for desorption into the gas phase or diffusion into the bulk. The activation energies for diffusion of atoms along a terrace from one step site to another are frequently half or less than half of the activation energies or heats for desorption into the gas phase (*11*). Therefore, one may assume equilibrium among molecules in the various surface sites in most circumstances. This is forced on the system by the long residence times, τ, due to the large desorption energies

$$\tau = \tau_0 \exp \Delta E/RT$$

where τ_0, which is associated with surface atom vibrations, is frequently of the order of 10^{-12} second; ΔE is the desorption energy; T is the surface temperature; and R is the gas constant. Thus the surface may be viewed as a two-dimensional phase that is well protected from exchange with the gas or the bulk by large potential energy barriers, while transport and chemical exchange along the surface are facile. There are systems and experimental conditions, of course, where the two-dimensional phase approximation is not appropriate. Surface reactions at high T or exothermic reactions where much of the chemical energy may be retained by the surface species would belong to this category.

The surface free energy is positive. The energy necessary to create a unit area of the surface is always positive. Thus a solid or a liquid would have a lower total energy without a surface, if this were possible. The magnitude of the surface free energy (or surface energy), σ, depends on the chemical bonding of the solid or liquid. For metals, the surface energies are around 10^3 erg/cm^2, which is about 14 kilocalories per mole for surfaces with an atom concentration of 10^{15} cm^{-2}. For most ionic solids and oxides the surface free energies are a few hundred ergs per square centimeter; for water, 82 erg/cm^2; and for hydrocarbons, considerably less (*12*). The surfaces of fluorinated hydrocarbons are among those with the lowest free energy.

There are some very important consequences of this positive surface free energy. Condensed systems in equilibrium minimize their surface free energy by assuming shapes with the smallest possible surface area. Also, the surface is covered at all times with a substance that minimizes its free energy. In multicomponent systems the constituent that has the lowest surface free energy segregates to the surface. As a result, alloys have different compositions in the surface than in the bulk (*13, 14*). Wetting or lack of adhesion is determined by whether the spreading of one type of molecules on the surface reduces or increases the total surface free energy. The difficulty of achieving homogeneous nucleation and the ability to maintain supersaturated systems are both due to the high positive surface energy term $4\pi\sigma r^2$, which for particles of small radius, r, overrides the negative volumetric free energy term (proportional to r^3) that provides the driving force for growth near equilibrium (*15*).

The surface dipole. There is a net charge separation at the surface due to the anisotropic environment of the surface atoms. On one side of the surface there are atoms of the same type, and on the other there are atoms of a different charge density or a vacuum. In the bulk of a metal, for example, each electron lowers its energy by pushing the other electrons aside to form an "exchange correlation hole." This attractive interaction, V_{exc}, is lost when the electron leaves the solid, so there is a sharp potential barrier at the surface. Quantum mechanically, the electrons are not totally trapped at the surface and there is a small probability for them to leak into the vacuum. This charge leakage creates a surface dipole, V_{dip}, that modifies the barrier potential. The work function, ϕ, is given by $\phi = V_{\text{exc}} + V_{\text{dip}} - E_{\text{F}}$, where E_{F} is the Fermi energy. This dipole is even more important at the surface of an ionic solid, where there is a large polarization due to the localized ion charges. Surface dipoles exist for all types of solids and give rise to important bonding and electrical properties. One of the practical applications of the surface dipole is at colloid surfaces, where the electrical double layer that forms because of the separation of surface charges is responsible for keeping the colloid system stable (*16*). Breakdowns of the electrical double layer by agitation or by ion exchange lead to precipitation and coagulation of the colloid system. This phenomenon is of major consequence in soil chemistry and in human biology, to mention two important colloid systems.

Surface Composition and Valence

Electron spectroscopic investigations of one-component systems have revealed the segregation of a large variety of impurities to the surface from the bulk of the condensed phase. The driving force for this is the change of chemical bonding of the impurities or the minimization of the surface free energy, as mentioned above. Carbon, hydrocarbons, sulfur, oxygen, calcium, aluminum, and silicon are among the most common impurities that contaminate the surface. Their removal is a prerequisite to obtaining clean surfaces to be used as reference states for surface studies. Ion bombardment and chemical reactions are used most frequently for this purpose. Surface segregation of one constituent in a multicomponent system is commonly observed (*13, 14*). Two-component alloy systems that obey regular solution thermodynamics or alloy systems with complex phase diagrams have been studied most thoroughly (*14, 17*). Several thermodynamic models have been proposed to predict surface enrichment (*13, 14*).

There are three experimental parameters that influence surface composition: (i) the relative surface tensions of the pure components, (ii) the heats of formation of the binary compounds that may form, and (iii) the lattice strain energy that is due to the mismatch of the atomic sizes of the constituents. Large values of (i) and (iii) give rise to surface compositions that are different from the bulk stoichiometry, whereas a large negative value of (ii) compared to (i) and (iii), which results in compound formation, stabilizes a bulklike composition in the surface region (*14, 17*). Significant variations of surface composition with temperature have been reported. An interesting phenomenon occurs for small particles in multicomponent systems. In the limit of very small particle size where all the atoms are located on the surface (dispersion = surface atoms/total number of atoms = unity), any variation in composition between the surface and the bulk should disappear. There is evidence, however, for the formation of surface compounds in this circumstance. Bimetallic systems, such as ruthenium-copper or iridium-gold, that exhibit very low solubility in the solid state become miscible and form solid solutions when deposited as small particles with near-unity dispersion (*18, 19*). Research into the phase diagrams of these surface phases is a fertile area that will influence catalysis as well as powder metallurgy.

A two-component system becomes a three-component system in the presence of an adsorbate. The appearance of the third component on the surface may markedly affect the surface composition. Carbon monoxide, for example, has been found to pull palladium onto the surface of a silver-palladium alloy that in the absence of CO is enriched by almost a monolayer of silver (*20*). Other impurities such as oxygen and carbon have similar effects and will change the surface composition as the ambient atmosphere becomes reducing or oxidizing.

Nonstoichiometry has frequently been observed in the surface layer in compounds with high heats of formation. Ionic solids (alkali halides and lithium hydride) have an excess of one of the ions—the cation in most cases. Compound semiconductors as well as oxides show detectable nonstoichiometry when heated in a vacuum at elevated temperatures (*21, 22*). Perhaps one of the most important consequences of a large deviation from stoichiometry in the surface layer is the appearance of unusual oxidation states. Large concentrations of Ti^{3+} appear to be stabilized in the TiO_2 and $SrTiO_3$ surface layers, and there is evidence for the presence of Al^{2+} and Al^+ oxidation states in Al_2O_3 crystal surfaces (*23, 24*). These oxidation states are stabilized only in the surface environment and have unique chemical and electrical properties.

Structure of Surfaces

Clean surfaces. Studies of the structure of clean surfaces by low-energy electron diffraction (LEED) have revealed several phenomena that were not known previously (*25*). Atoms in the surface layer and in the near-surface region may "relax" into new equilibrium positions. For several systems such shifts in the location of surface atoms yield a new ordered surface structure, and in these cases the surface rearrangement is called reconstruction. Finally, crystal surfaces that are characterized by high Miller indices assume surface structures that consist of ordered steps, frequently of monatomic height, separated by terraces of the same average width. Often there are ordered kinks in the steps.

Although the surface unit cell remains unchanged, the relaxation is verified by surface structure analysis with the LEED beam intensities. The theory of LEED has been developed to the point that the location of the surface atoms can be determined with a high degree of reliability in most cases (*22, 26*). Relaxation appears to be marked for the Al(110), Mo(100), and W(100) surfaces, which show contraction of the first layer toward the second layer by 15, 12, and 6 percent of the interlayer distance, respectively. For other crystal faces, such as Ni(111) and Pt(111), however, the relaxation is negligible. Reconstruction is detected at elemental semiconductor surfaces (silicon and germanium) and at polar surfaces of compound semiconductors (*22, 26*). Also, several metals have reconstructed surfaces at all temperatures up to the melting point [Pt(100), Pt(110), Au(100), Au(110), and Ir(100), for example], while others reconstruct only at low temperatures [W(100) and Mo(100)] (*23*). It has been difficult to analyze the structures of reconstructed surfaces because of the complexity of many of the unit cells. However, drastic relocations of atoms in the first and perhaps the second layer are necessary to explain the observed surface structural changes. The anisotropic surface environment necessitates atomic relocation in order to optimize chemical bonding and lower the total surface energy. In the case of compounds, nonstoichiometry and relaxation are detected for alkali halide surfaces, while reconstruction and nonstoichiometry are detected for compound semiconductor and oxide surfaces. Ordered vacancy structures appear on vanadium oxide and titanium oxide (*23, 24*) surfaces that are stabilized by simultaneous changes of the oxidation states of large concentrations of surface atoms. The study of surface structural changes as the bulk of the solid undergoes phase transformations is an interesting area of research. The surface phase transformation of cobalt as it changes from hexagonal close-packed to face-centered cubic symmetry and that of NiO as it undergoes antiferromagnetic transformation at the Néel temperature have been investigated (*27*).

Inert gas crystals can be grown by slow condensation on ordered crystal surfaces at low temperatures and their surface structures can be studied (*28*). Using a similar technique of epitaxial vapor deposition, molecular crystals can be grown and their surface structures studied by LEED. Ice, naphthalene, benzene, paraffin, phthalocyanine, and amino acid crystal surfaces were investigated in this manner (*29*). For most larger molecules the orientation and structure of the growing surface may be determined by the orientation and structure of the first monolayer, which repeats itself during growth. This phenomenon is pseudomorphism and, depending on the atomic structure of the substrate and the first monolayer, molecular crys-

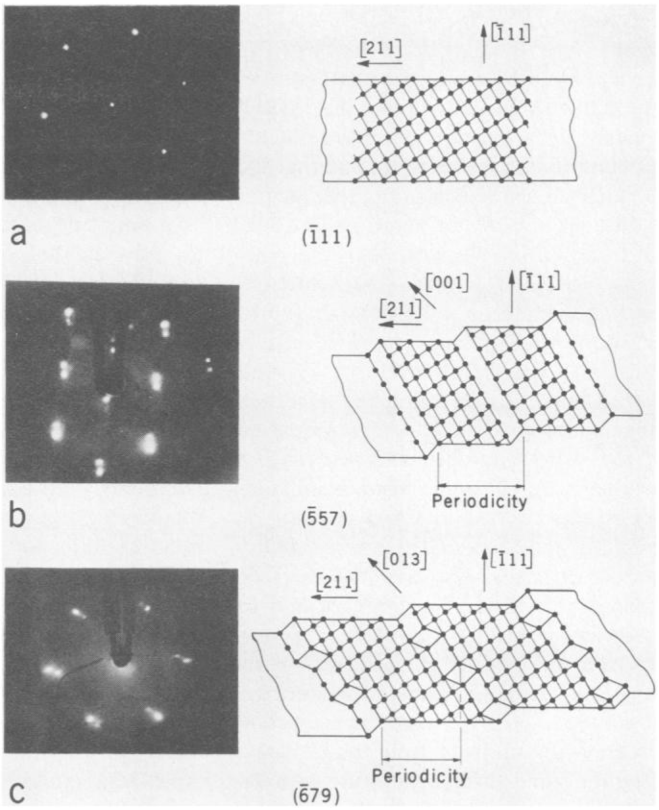

Fig. 3. LEED patterns and schematic representations of three types of face-centered cubic crystal surfaces. (a) The ($\bar{1}11$) orientation containing less than 10^{12} defects per square centimeter. (b) The ($\bar{5}57$) surface with 2.5×10^{14} step atoms per square centimeter and six-atom-wide terraces between steps. (c) The ($\bar{6}79$) surface with 2.3×10^{14} step atoms and 7×10^{13} kink atoms per square centimeter. The average spacing between steps is seven atoms; that between kinks is three atoms.

tal surfaces with a variety of structures can be prepared (*29*).

Ordered surface irregularities: steps and kinks. By cutting or cleaving a crystal surface along the directions of highest atomic density (lowest Miller indices) an atomically homogeneous surface can be obtained. The (111) crystal face of face-centered cubic solids (Ni, Ag, Pt, Ir, Au, and so on) is such a surface, and its atomic structure deduced from LEED patterns is shown in Fig. 3a. Such a surface may exhibit many macroscopic irregularities when observed with an optical microscope or a scanning electron microscope. On the atomic scale, however, there are large ordered domains, with most of the surface atoms occupying their sixfold rotational symmetry equilibrium positions. By cutting crystals along planes of lower atomic density (higher Miller indices), one can prepare crystal faces that exhibit ordered step and kink structures, as shown in Fig. 3, b and c. By changing the cutting angle, the terrace width and simultaneously the step density can be altered. Surfaces with step densities as high as 33 percent of the total number of surface sites can be prepared (*30*). These step or kink structures, once prepared, have remarkable thermal stability. Although structural changes do take place in the presence of an adsorbate (such as carbon or oxygen) that alters the step heights and terrace widths, the structure that characterizes the clean surface reappears when the adsorbate is removed. Many stable surfaces have ordered kink and terrace structures with ordered monatomic steps; other surfaces are unstable in this configuration (*30*). The reversible changes of surface structure that take place on adsorption or removal of surface impurities are of great importance in studies of the catalytic activity, redispersion, and sintering of small particles. The surface irregularities, steps, kinks, and atoms in unusual oxidation states that appear at these defects play dominant roles in heterogeneous catalysis and other gas-solid surface reactions.

Structure of adsorbed monolayers. The surface concentration of adsorbates, (A), in equilibrium depends on the pressure of adsorbates, P_{eq}, and on their surface residence times (*31*). Far from a monolayer coverage, the concentration of adsorbates for the homogeneous surface is given by $(A) = F\tau$, where the flux to the surface $F = P_{eq}/(2\pi MRT)^{1/2}$, M being the molecular weight of the adsorbate. Since τ depends exponentially on the heat of adsorption, (A) at a particular temperature depends on the pressure over the system and the heat of adsorption. The heat of adsorption does not remain constant with coverage, of course, but changes as a result of adsorbate-adsorbate interactions. Since the surface is heterogeneous, the highest binding-energy sites that are available are likely to fill up with adsorbates first. For weakly held adsorbates the experiments are carried out at low temperatures (below 200 K), while strongly held adsorbates may yield monolayer coverages at 300 K or above (*31*). Because of the differences of experimental conditions, the former is called weak physical adsorption and the latter chemisorption; the division is arbitrary as bonding interactions vary smoothly and gradually from system to system.

Surface structure analysis has been carried out for several adsorbate systems. In most cases the adsorbates have been atomic and the locations of the atoms have been determined. Often adsorbed atoms occupy sites of the highest rotational symmetry and the adsorbate-substrate bond distance corresponds to the sum of the covalent radii (*31*). For example, oxygen, sulfur, selenium, and tellurium on Ni(100) crystal faces behave this way. In other instances the bonding is more unusual. Nitrogen atoms, when adsorbed on titanium metal surfaces, are located below the surface and not on top of the metal atoms. When oxygen is adsorbed on Fe(100) it forces the metal atoms to rearrange and assume new equilibrium positions (*31*). Adsorption-induced reconstruction is certainly a possibility in systems where the adsorbate-substrate bonds are stronger than the substrate-substrate bonds.

Perhaps the most striking characteristic of adsorbate-substrate systems is the predominance of ordering in the monolayer. Adsorbed atoms or molecules often form ordered islands at low coverages that grow and may change structure with increasing coverage. Order-order and order-disorder transformations in the monolayer are frequently observed. More than 300 monolayer surface structures have been reported and tabulated (*31*). Rules of ordering have been proposed that in some cases permit prediction of the size and orientation of adsorbate surface unit cells (*31*). Structure analysis has been carried out for only two molecules (*32*). The first, C_2H_2 on Pt(111), has a unit cell that is twice as large as the unit cell of the platinum substrate and is parallel to it. At 300 K, C_2H_2 adsorbs in such a way that the molecule is localized almost on top of the platinum atom at a Pt–C distance of 2.5 Å. At 375 K the location of the molecule changes with respect to the metal atom in the substrate, although the unit cell remains unchanged. Analysis of the diffraction beam intensities indicates that the molecule is located in a triangular site at a nearest Pt–C distance of 2.0 Å and is bound effectively to three metal atoms much more strongly than before. The second molecular system that has recently been studied is CO on the Ni(100) crystal face. It appears that the molecule is bound to one nickel atom and that the CO internuclear axis is not perpendicular to the surface but at some angle to it. High-resolution electron loss spectroscopy (HRELS) is used for structural analysis in addition to LEED (*33*). It provides the vibrational spectra of adsorbates as a function of (*A*) and *T*. With this technique ordering in the adsorbed layer is not necessary for determination of the surface structure. Variations of bonding with (*A*) and *T* have been studied by this method in a few systems. A great advantage of HRELS is its ability to detect hydrogen on the surface through its vibration against carbon or substrate atoms. Angle-resolved photoelectron spectroscopy and ion scattering can also be used for surface structure determination (*33*). Perhaps the important direction for the near future is to determine the same surface structure by a variety of techniques in order to calibrate them against one another. These studies reveal the richness and complexity of structure of adsorbed monolayers, which varies with temperature and coverage and from crystal face to crystal face, and they will no doubt produce many surprises in the future.

Surface Chemical Bond

A great deal of information has emerged from surface diffraction, vibrational spectroscopy, and electron spectroscopy studies of the nature of the surface chemical bond in several chemisorbed systems. Perhaps the most remarkable finding is the rapid change in character of this bond with temperature (*34*). Any reactive molecule (C_2H_4, for example) may be adsorbed intact on any chemically active substrate (iron or tungsten, for example) as long as the temperature is low enough (about 100 K). As the surface is heated gradually, selective bond-breaking processes take place at different temperatures (*34*). For C_2H_4 on tungsten, C–H bonds break first at 150 K and the molecule is converted to C_2H_2. Further heating to 300 K removes the other two hydrogen atoms and C_2 units form. Finally, heating to 1100 K dissociates the carbon dimers as well. On iron surfaces C–C bond breaking occurs first with increasing temperature, and there is evidence for the presence of CH_2 species from angle-resolved photoelectron spectroscopy. Acetylene, on the Pt(111) surface, changes its bonding drastically as the temperature is increased from 300 to 375 K. Diatomic molecules (O_2, H_2, CO) undergo dissociation with increasing temperature. Carbon monoxide, for example, adsorbs as a molecule on nickel surfaces at 300 K. It dissociates, however, when the adsorbed layer is heated to about 500 K.

It appears that even the most homogeneous single-crystal surface has many binding sites. Some of them, however, are not accessible to the adsorbed molecules at low temperatures. A small potential barrier of height *kT* has to be overcome before the molecule assumes its more strongly bound location, where bond breaking or molecular rearrangement occurs. Thus, even though the breaking up of the molecule and the formation of strong substrate bonds with the atomic constituents is thermodynamically feasible (for example, $C_2H_2 + 4Fe = 2FeC + 2FeH$ has a negative free energy of reaction) it will not occur at all at low temperatures and it takes place sequentially as the temperature is raised.

Irregularities on transition metal and oxide surfaces have the ability to efficiently break strong chemical bonds (H–H, C–H, C–C, C=O, and so on) that would otherwise remain intact in the absence of defects on the surface. Heats of chemisorption also appear to be higher at steps in some cases. In general, the chemical bonds of most adsorbates appear to be very sensitive to structure. In Fig. 4 heats of chemisorption of oxygen and carbon monoxide are plotted for various crystal faces of different elements in the periodic table. There are several binding states for a given crystal face, with heats of chemisorption that vary by a factor of 2 or more. There is indeed no such thing as a single binding energy for a particular molecule and a particular surface, as has been commonly assumed. The various binding states are filled with increasing surface coverage at any temperature, and the nature of the binding states may also change with increasing temperature.

Both the structure sensitivity of the surface chemical bond and its temperature dependence indicate the predominance of localized interactions in determining the nature and strength of the bond. Indeed, recent photoelectron spectroscopy studies revealed great similarities between the electronic structure of carbon monoxide adsorbed on metal surfaces and the electronic structure of metal carbonyl clusters with four metal atoms in the molecule (*35*). It appears that the chemical bonding of metal cluster–ligand systems will provide insight into the surface chemical bonds for many substrate-adsorbate systems. The predominance of ordering in the adsorbed monolayer and its island-like growth indicate the importance of adsorbate-adsorbate interactions. It is difficult to assess the relative importance of these interactions compared to adsorbate-substrate interactions for the surface chemical bond.

Dynamics of Gas-Surface Interactions

Surfaces are primarily used to carry out chemical reactions or as the first line of defense of the condensed phase against external chemical and mechanical forces. In either case, study of the dynamics of surface reactions is an integral part of the characterization of the chemical properties of any surface (*36*, *37*). In attempting to understand surface chemical reactions on the molecular scale, we may arbitrarily divide gas-surface interactions into two types: (i) those involving nonreactive energy transfer between the gas molecules and the surface, and (ii) reactive solid-gas interactions. In these studies we try to understand the nature of energy accommodation between translational (T), rotational (R), and vibrational (V) modes of the gas molecules with the vibrating surface atom (V_s). Then the minimum residence time necessary for an elementary surface reaction to take place is determined, along with the reaction probability. Finally, we investigate how the available energy is partitioned among the reactants, the products, and the surface during the surface reaction. The energy transfer information obtained on the molecular scale is then related to the macroscopic reaction rates and other kinetic parameters and to the product distribution.

To study gas-surface energy transfer and the nature of elementary surface reactions, we must carry out experiments at low pressures or relatively high surface temperatures. This allows variation of the surface coverage from 1 percent to a complete monolayer and preferably permits only a single collision of the incident molecules with the surface before the energy content of the desorbing species is analyzed. One of the most powerful techniques for this purpose is molecular beam–surface scattering (*27*). A well-collimated beam of molecules of known velocity impinge on the surface at various angles of incidence. The surface may be one face of a single crystal with known atomic surface structure and composition located in the center of an ultrahigh-vacuum chamber to maintain surface cleanliness during the experiments. The exiting molecules, after scattering, are detected in a mass spectrometer that can be rotated to detect their angular distribution. By suitable chopping of the incident and exiting molecular beams, the surface residence time and the velocity are determined by time-of-flight analysis.

These studies of nonreactive gas-surface systems reveal relatively poor T-V_s energy transfer in single scattering from a clean surface (*38*). This means that an exiting molecule does not efficiently remove the thermal energy of a heated surface. When the surface is covered with a monolayer of carbon monoxide or roughened on the atomic scale, the T-V_s energy transfer markedly improves. The R-V_s energy transfer appears to be much more efficient (*28*). The large isotope effect observed when H_2, D_2, and HD molecules are scattered is accounted for by the relative ease of excitation of rotational modes of the heavier D_2 and HD molecules compared to the H_2 molecules. The V-V_s energy transfer processes have not been investigated thoroughly yet. Although much of the experimental information was obtained through studies of the angular distribution of the scattered atoms and molecules, recent technological advances have made it possible to construct instruments for both time-of-flight velocity and angular distribution analysis.

Elementary catalyzed surface reactions such as the H_2-D_2 exchange and the dissociation of diatomic (H_2, O_2) and polyatomic (N_2O, HCOOH) molecules have also been studied by using this technique, and the kinetic parameters (preexponential factors, activation energies, rates as a function of temperature) have been determined (*37, 39*). The kinetics of elementary gas-solid chemical reactions where the surface atoms are the reactants (for example, $2C + H_2 = C_2H_2$) have also been investigated (*37, 39*). High reaction probabilities (in the range of 0.1 to 1.0) can be obtained on single scattering, and the surface residence times of the reacting molecules are long, in the range 10^{-2} to 1 second, for endothermic or athermic surface reactions. For exothermic reactions, such as atom recombinations, where excess chemical energy is available for partitioning among the product molecules and the surface, the residence times are likely to be much shorter. However, this has not yet been verified by experiments. Another technique, which involves a rapid jump in the temperature to react and desorb the molecules from the surface, has also been sucessful in obtaining detailed kinetic information about elementary surface reactions and indicating the presence of realistic surface reaction intermediates (*37, 39*).

The surface reactions studied so far are very sensitive to the atomic surface structure and surface composition. Considering the sensitivity of the surface chemical bond to these parameters, these findings are not surprising. By changing the atomic step density, the reaction probability for H_2-D_2 exchange at platinum surfaces can be increased by an order of magnitude (*37, 39*). Contamination of the nickel surface by small amounts of carbon can completely change the nature of the reaction intermediates and the product distribution during the decomposition of HCOOH (*37, 39*). The kinetic data (preexponential factors and activation energies) permit one to identify the rate-determining steps and changes of the rate-limiting processes as the experimental conditions (temperature, surface coverage, structure, and composition) are altered.

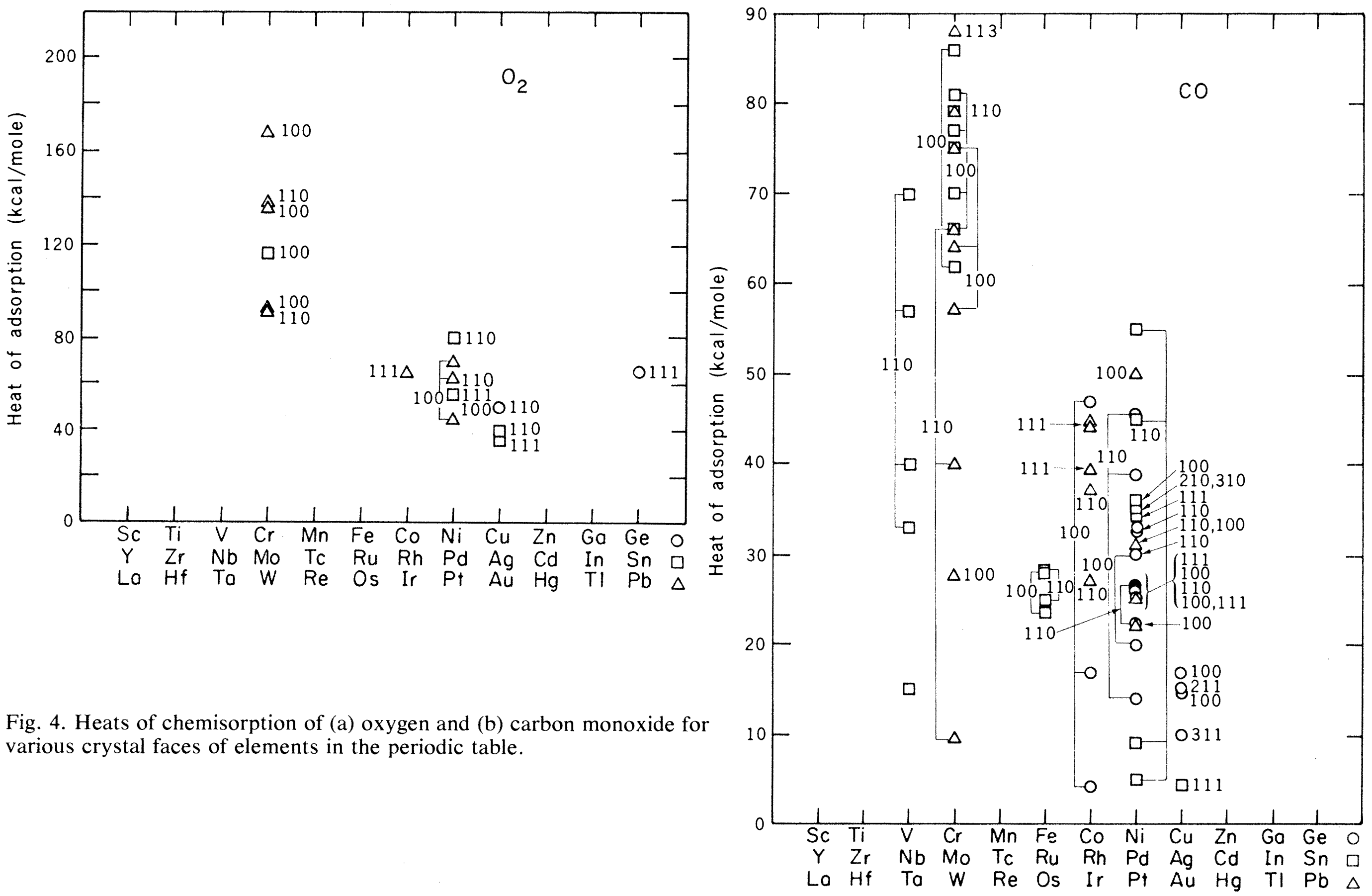

Fig. 4. Heats of chemisorption of (a) oxygen and (b) carbon monoxide for various crystal faces of elements in the periodic table.

Studies of Surface Reactions at Low and High Pressures

Although low-pressure single-scattering reaction conditions are of great value in deciphering the elementary surface processes, the experimental conditions are far removed from those utilized in practical surface reaction studies, where instead of reactant pressures of 10^{-8} to 10^{-5} torr, pressures of 10^3 to 10^5 torr are employed. The reaction mechanisms are expected to change significantly with pressure as the surface coverage as well as the surface residence times of adsorbates vary. To bridge the pressure gap, new techniques have been developed in which the small (1 cm^2) catalyst sample is enclosed in a cup in the middle of an ultrahigh-vacuum chamber (*40*). Once enclosed, the sample can be pressurized up to 100 atm ($\sim 10^5$ torr) and the surface reactions can be followed by using a gas chromatograph as a detector. The surface structure and composition can be characterized before and after the high-pressure study without removing the sample from the controlled-atmosphere enclosure. The catalyzed reactions of hydrocarbons on platinum surfaces and the hydrogenation of carbon monoxide on rhodium and iron have been studied in this way (*40*).

By determining the kinetics of the reactions as a function of pressure, the reaction mechanisms at low pressures (molecular beam–surface scattering experiments) and at high pressures (practical catalytic reaction conditions) can be correlated. In addition, the kinetics of high-pressure catalyzed reactions on well-characterized surfaces can be correlated with data on catalyzed reactions on dispersed systems with large surface areas. These studies begin to reveal the ingredients of selective heterogeneous catalytic processes. For example, surface irregularities on platinum surfaces were found to play important roles in hydrocarbon reactions (*3–6, 9, 19, 41*). The H–H and C–H bonds break readily at steps, while the C–C bonds break more readily at kinks, which break H–H and C–H bonds as well. Thus, by blocking the kink sites with other metal atoms or by impurities, hydrogenolysis is suppressed while dehydrogenation and isomerization are largely unaffected, since the kink concentration is only about 5 to 10 percent of a monolayer. The presence of 10 to 20 percent of a monolayer of oxygen was found to increase the reaction rates significantly. Important surface reactions such as the dehydrocyclization of *n*-heptane to benzene or toluene can be carried out only if oxygen is present at the platinum surface in addition to the surface irregularities. Clean iron and rhodium were found to be mediocre methanation catalysts in the $CO + H_2$ reaction, while rhodium and iron industrial catalysts produce alcohols, aldehydes, and acids (*3–6, 9, 19, 41*). It has become apparent from these studies that the clean metals are not the practical catalysts, but additives (promoters) such as potassium and compounds (carbides or oxycarbides) produced in the reaction mixture on the surface are responsible for much of the observed catalytic reactivity. As a result of these and other molecular investigations with well-characterized surfaces, heterogeneous catalysis is rapidly becoming a science.

A great deal of interest has developed in relating homogeneous and heterogeneous catalysis (*42*). The structure and chemical bonding of organometallic clusters are being correlated with the structure and bonding of organic adsorbates on surfaces. The activities of metal-ligand systems and surfaces in the same displacement and catalyzed reactions are being scrutinized (*42*). These studies promise a better understanding of the chemistry of both homogeneous and heterogeneous systems and perhaps of how to tailor them to obtain the desired chemistry.

Thermodynamically uphill photon-assisted reactions are being investigated at solid-gas and solid-liquid interfaces (*24, 43*). The reactions studied include the dissociation of water to hydrogen and oxygen and reactions of CO_2 and H_2O. Light of band-gap radiation, when incident on a suitable semiconductor or oxide surface (for example, $SrTiO_3$, TiO_2, or GaP), generates electrons and holes, which can oxidize and reduce the adsorbates (*24, 43*). In addition to indirect excitation of adsorbed molecules by charge transfer from the surface atoms, the adsorbates may also be excited by light directly. These important classes of surface reactions will receive increasing attention in the near future.

Other Directions for the Near Future

Surface science has developed rapidly in obtaining an understanding at the molecular level of the structure, bonding, and reactivity of many surface-adsorbate systems. However, there are important areas of concern in surface science where very few inroads have been made. Perhaps the most important are the solid-liquid and solid-solid interfaces. Modern electron- and ion-scattering techniques, which are excellent for studies of the solid-gas interface, cannot provide information about the interface of two media with nearly equal atomic densities. Most of the surface chemistry in biology, electrochemistry, and colloid chemistry takes place at the solid-liquid interface, and many of the mechanical properties of solids are controlled by properties of solid-solid interfaces. Enzyme catalysis and heterogeneous catalysis are areas of research where correlations are desirable and should be possible. Yet progress in these areas must await the development and utilization of new techniques for probing these interfaces on the molecular scale. Various light-scattering techniques with high-intensity x-rays or ultraviolet radiation appear to be promising for this purpose, and we will see increased activity in this frontier area of research in the near future.

There is a schism among surface chemists. There are those who study and determine macroscopic surface parameters in various important subfields (for example, rates of surface reactions over heterogeneous catalysts or at electrode surfaces, or interfacial tensions determined by contact angle measurements). Then there are those who concentrate on atomic-scale determinations of the surface structure and composition by low-energy electron diffraction and other electron- or ion-scattering techniques. *Perhaps the most significant developments occur as the molecular and macroscopic properties of surfaces are correlated.* The synthesis of these two approaches, I believe, will be of the greatest benefit to surface science and to technologies that are now based on surface properties.

The most significant role of modern surface science is in the energy sciences. Virtually all energy conversion schemes and energy storage systems involve surface science. Recently a series of nine workshops were organized by the Materials Science Program of the Basic Energy Sciences Division of the Department of Energy to assess the status and direction of various subfields of materials research in the areas of fossil, nuclear, fusion, solar, and geothermal energy conversion, and in conservation. Research in surface science appeared at the top of the list of priorities in the workshop reports. The mechanical properties of solids related to surface properties, surfaces under radiation-damage conditions, chemical corrosion and inhibition, catalyzed liquefication and gasification of coal, and removal of nitrogen from coal by surface chemistry are just a few of the many long-term problems of energy conversion that research in surface science can help to resolve. Since energy—its production, conversion, and control—has been recognized as a societal problem, physical sciences and engineering will become increasingly involved in research and development in this area over the next several decades. Surface science has always attracted talented scientists and engineers, but it already lacks people in sufficient numbers to cover the areas that are the basis of present-day technology. We are far from "critical mass" when it comes to educating and carrying out research in the field. With the heightened activity in energy sciences, the lack of people trained in surface science will become even more acute. It is likely that most of the positions in the field that become available will be filled by those who retrain and enter the field of surface science from other fields. No doubt surface science will provide challenges and opportunities for first-class frontier research as well as for the development of important new technologies for many years to come.

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