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CORRELATIONS BETWEEN THE STRUCTURE AND REACTIVITY AT
SOLID-GAS AND SOLID-LIQUID INTERFACES

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I am greatly honored to be the Lecturer for the 50th national meeting of this distinguished and successful society. I would like to start by making a prediction: I assert that the new developments in the fundamental understanding of electrode processes and of chemical phenomena that takes place at the solid-liquid interface will come from correlations with studies of equivalent processes at the solid-gas interface.

Now let me explain why I believe this to be the case.

Over the past decade there has been a dramatic improvement of our knowledge of surface phenomena on the atomic and molecular scale at the solid-vacuum and solid-gas interfaces. Techniques that use the surface scattering of electrons, ions and molecules has become available that determine the atomic and electronic structure of the surface monolayer, its composition and valency of surface atoms. Some of the more widely used techniques are listed in Table I. Low-energy electron diffraction (LEED) is utilized to determine the structure of the clean surface and of the monolayer of ordered adsorbates.¹ Auger electron spectroscopy² (AES), photoelectron spectroscopy³ (XPS) are used to determine the chemical composition and valency of surface atoms; while ion scattering spectrometry⁴ (ISS) and secondary ion mass spectrometry⁵ (SIMS) are utilized to determine the composition in the submonolayer region. Although all of these techniques, except LEED, can be used to study surfaces, regardless of

their atomic structure (polycrystalline foils, evaporated films, liquids or powders), many of the major advances in our understanding of the chemistry of surface atoms has come from studies of well-ordered crystal faces of single crystals. Using crystals we can vary the concentration of different surface sites that are distinguishable by the number of nearest neighbors. The three types of surfaces that exhibit the various surface sites which are important in studies of chemisorption and surface chemical reactions are shown in Fig. 1.⁶ Figure 1a shows a low Miller Index (111) surface in which most of the surface atoms are in locations where they are surrounded by six nearest neighbors in the surface plane. Although the low Miller Index surface may be rough on a macroscopic scale, full of defects that are induced by the presence of dislocations in the bulk, the surface can be prepared in such a way that most of its atoms are in their equilibrium, high symmetry sites. Figure 1b shows a surface with a high density of steps of atomic height. In such a surface there are large concentrations of surface sites of two types: step atoms and atoms in terraces. The former has less number of nearest neighbors. Many high Miller Index surfaces exhibit this surface structure.⁷ Finally Fig. 1c shows another type of high Miller Index surface that has three types of surface sites in high concentrations: terrace and step atoms and atoms at kinks in the steps. Crystal surfaces can be cut and prepared in which every third atom in the step is a kink atom. One example of this is shown in Fig. 1c.

There is a great deal of experimental evidence accumulating in recent years that indicates that the chemical activity of these various surface sites (kinks, steps and terrace atoms) are different.^{8,9} They

form chemical bonds that differ in strength by about ± 5 kcal/mole¹⁰ or carry out surface reactions on transition metal surfaces with different rates and selectivity.¹¹ Of course, when a polycrystalline surface (wire or foil or thin film) is studied, one detects a chemical behavior (heat of chemisorption, reaction rate and product distribution) that is integrated over all these surface atoms. Thus, identification of the various reactive surface sites cannot be made in this circumstance.

At the same time the surface diagnostic techniques were developing that are listed in Table I that, by and large, scrutinize the surface in static, low-pressure conditions, several techniques were developing in my laboratory for kinetic studies of surface reactions under low pressure and high pressure conditions.^{12,13} Using suitable apparatus, one can measure the rate and product distribution in surface reactions while also monitoring the structure and composition of the surface using small surface area (approximately 1 cm^2) single crystal samples. This way the relationships between the reactivity of the surface and the structure and composition can be determined.

The apparatus that is used to study high pressure gas reactions and is also suitable to study surface reactions at the solid-liquid interface, is shown in Fig. 2.¹³ The sample (polycrystalline foil or single crystal) is located at the center of the axis of the ultrahigh vacuum chamber and it is accessible to the LEED, AES, ion bombardment and mass spectrometry facilities. It is spot-welded to two heating rods which are attached to copper conducting bars in a quartz insulating tube. This is attached to a teflon compression sealed stainless steel shaft which allows 180° rotation of the sample at any pressure (10^{-9} to 10^5 torr). The rotary

motion is necessary to clean the sample with the ion gun then rotate it for LEED, AES and thermal desorption measurements. The sample may be enclosed by a small high pressure cell which is operated by hydraulic pressure from above and engages a copper sealing gasket below the sample. The internal volume of this isolation chamber is small, about 30 cm³. Access to the central chamber is made via inlet ports running down the axis of the tube. The sample is heated resistively via the feedthroughs in the lower portion of the manipulator and the temperature is measured with a thermocouple spot-welded to the sample. Gases are admitted to the circulation loop and reaction cell from a suction pumped manifold and a small metal bellows diaphragm pump is used to circulate gases around the loop. The gases pass through a low-internal-volume gas sampling valve which extracts .1 mm of gas for gas chromatographic analysis.

At present this apparatus is being used to study the hydrogenation of carbon monoxide at both low and high pressures (as high as 100 atm) on small surface area metal surfaces.¹⁴ There is no reason why an apparatus of this type could not be adapted for studies of the solid-liquid interface. The liquid could readily be introduced and then pumped out after the studies and the surface can be studied by the various surface diagnostic techniques that are listed in Table I. This apparatus or similar types will be the instruments, I believe, that will permit us to develop the correlations between surface phenomena that occur at the solid-liquid and solid-gas interfaces.

Below I briefly review our present view of the atomic and electronic structure of surfaces and adsorbates, the surface composition of binary alloy systems as it emerges from modern studies of the solid-vacuum and

solid-gas interfaces. Then I shall review some of the surface reaction studies that have been carried out recently to correlate the reactivity of the surface with its structure and composition. Finally, I shall propose various research projects that would be of importance in order to begin to correlate surface phenomena at solid-liquid and solid-gas interfaces.

Atomic Structure of Clean Solid Surfaces as Determined by LEED

The atoms at the surface are in an asymmetric environment. They are surrounded by atoms in the surface layer and from beneath but there are no atoms above them. This surface environment has also lower symmetry than that provided for atoms in the bulk. The structural asymmetry experienced by atoms at the surface have a major effect that leads to surface reconstruction: atoms in the surface may move into new equilibrium positions that provide higher symmetry or greater overlap of available positions.

a) Surface reconstruction. There are several types of surface reconstruction observed for clean solid surfaces. Many surfaces have atomic structures that are different from that expected from the projection of the X-ray bulk unit cell. The surface atoms assume new equilibrium positions by out-of-plane buckling or by relaxing inward (contraction) that often results in entirely different ordered surface structures. An example of this is shown in Fig. 3. The diffraction pattern and schematic representation shown here are characteristic of the surface structure of the (100) crystal face of platinum. This surface exhibits the so-called (5x1) surface structure.¹⁵ There are two perpendicular domains of this structure and there are $1/5$, $2/5$, $3/5$ and $4/5$ order spots between the (00) and (10) diffraction beams. The surface structure appears to be stable at all

temperatures from 25°C to the melting point although at elevated temperatures impurities from the bulk can come to the surface and cause a transformation of the structure to the impurity stabilized (1x1) surface structure. Preliminary calculations by Clark *et al.*¹⁶ and in this laboratory indicate that a model for Pt(100) in which the surface atoms assume a distorted hexagonal configuration by out-of-plane buckling is favored. The apparent (5x1) unit cell is then the result of the coincidence of the atomic positions of atoms in the surface, i.e., in the distorted hexagonal layer, with atoms of the undistorted second layer below. The (100) crystal faces of gold¹⁷ and iridium¹⁸ that are neighbors of platinum in the periodic table exhibit the same surface reconstruction and the same surface structure as that of platinum that is shown in Fig. 3. The (110) crystal faces of these three elements are also restructured¹⁹ and exhibit different unit cells than that expected from the bulk X-ray structure. On the other hand, the (111) crystal face of these three metals appears to have the same surface structure as that indicated by the bulk unit cell.

For semi-conductors, most crystal planes that have been studied show reconstruction.²⁰ Monatomic and diatomic semi-conductor surfaces have been investigated in large numbers and surface reordering has been observed for most of them. Frequently there are changes of surface structure with temperature that are often irreversible.

For many metal surfaces, the distance between the uppermost two layers, i.e., the z-spacing, is equal to that of the bulk value to within the estimated accuracy of about five percent. However, the Al(110)²¹, Mo(100)²² and W(100)²³ surfaces seem to show substantial contraction in

the upper layer z-spacing with respect to the bulk while retaining the (1x1) surface unit cell. A simple contraction or expansion of the interplanar z-spacing of this kind is usually termed a "relaxation."

For many diatomic solids there is non-stoichiometry in the surface layer, that is the surface composition may be different from that in the bulk.²⁰ Non-stoichiometry is apparently a major factor in the observed reconstruction of the polar faces of the III-V semi-conductors such as gallium arsenide, GaAs. The (111) face, for example, would ideally have all gallium atoms at the surface bonded to arsenic atoms immediately beneath the surface while the reverse would be true of the ($\bar{1}\bar{1}\bar{1}$) face. However, the ($\bar{1}\bar{1}\bar{1}$) surface has been found to lose arsenic at elevated temperatures and this is associated with the appearance of a new surface structure, while at low temperature another surface structure is arsenic stabilized.²⁴ Similarly, phosphorus is found to preferentially desorb at high temperatures from the gallium phosphides ($\bar{1}\bar{1}\bar{1}$) surface.²⁵ On the other hand, the gallium arsenide (110) surface, which has an equal number of gallium and arsenic surface atoms, does not exhibit reconstruction. A number of studies have pointed to possible non-stoichiometry in alkali-halide crystal surfaces also upon cleavage.²⁶ On oxide surfaces, such as aluminum oxide²⁷ and vanadium pentoxide,²⁸ changes in chemical composition and valency of surface atoms have been related to the formation of new surface unit cells.

Molecular crystals constitute a large and important group of materials that include most organic solids, but only very recently have the surface structures of some of these materials been investigated on an atomic scale by low-energy electron diffraction. Ice and naphthalene have been grown

by vapor deposition⁽²⁹⁾ and ordered surface structures of crystals of many other organic solids such as benzene, trioxene, n-octane, cyclohexene and methanol have been grown on metal substrates at low temperatures.⁽³⁰⁾ Phthalocyanine crystals have been vapor-grown on ordered metal surfaces.⁽³¹⁾ These large molecular weight, large size organic crystals exhibit a different kind of surface reconstruction. When copper phthalocyanine was grown on the copper (111) surface, the surface structure of the growing organic crystal layer did not resemble the structure of any of the simpler crystal planes in the bulk structure of the organic crystal. It appears that the ordered metal substrate predetermined the orientation and packing of the phthalocyanine monolayer, which in turn controlled the orientation and packing of the organic layer deposited on top of it. For large molecules, such as phthalocyanine, restructuring into a more stable crystallographic arrangement requires molecular rotation and diffusion processes that are too slow under conditions of crystal growth. Thus the molecules are frozen into a surface structure that is predetermined by the structure of the substrate and the first adsorbed organic monolayer.

b) Surface irregularities. The surfaces of real solids are atomically heterogeneous and not smooth as shown schematically in Fig. 4. There are several atomic sites present simultaneously that are distinguishable by their number of nearest neighbors. The symmetry of these low coordination number sites and their charge density are different from that of the sites on the smooth surface and are different from each other. As a result, large variation in chemical bonding of adsorbates at these different sites could occur. Indeed, there is an increasing body of experimental evidence

that indicate that atomic steps and kinks behave as different chemical entities at transition metal^{32,33} and semi-conductor surfaces,³⁴ forming chemical bonds of different strengths as compared to that of the atoms on the terraces.

Preparation of surfaces with a large concentration of stable and ordered irregularities (steps and kinks) can be carried out by cutting crystal faces along high Miller index directions. Stepped surfaces of several metals,³⁵ semi-conductors³⁶ and oxide surfaces³⁷ were prepared this way.

Charge Density at Clean Solid Surfaces

Let us consider an atomically smooth surface where each atom is in the same structural environment. The surface atoms have less nearest neighbors as compared to atoms in the bulk. As a result, electronic orbitals that are used for bonding of bulk atoms are available at the surface, giving rise to increased charge density. These localized unsaturated bonding orbitals are frequently called dangling bonds and the angular distribution of their charge density largely depends on the structural arrangement (packing of atoms, orientation) at the surface. There is excess free electron density at metal surfaces that is not localized at a given atom that gives rise to an induced surface dipole. The presence of this dipole is responsible for changes of the work function of metals from crystal face to crystal face. The formation of the surface dipole can be rationalized and demonstrated using the so-called jellium model. There are strong exchange correlation forces which act on the electrons in the solid due to their many-body coulomb interactions. In the metal interior each electron lowers its energy by pushing others away to form the exchange-

correlation "hole." This attractive interaction is lost when the electron leaves the solid so there is a sharp potential barrier at the surface. In the jellium model the positive charge density from the ion cores is smeared out over the atomic volume and the conduction electrons are free to respond to the surface barrier potential. At the surface, however, the electrons are not totally trapped and there is a small probability to leak out in the vacuum. This charge leakage creates a dipole effect which modifies the self-consistent surface barrier potential. This dipole creates an additional electrostatic barrier for the electrons in the solid, V_{dipole} , so that the total barrier, $V_{\text{total}} = V_{\text{exchange}} + V_{\text{dipole}}$. This gives the work function, $\phi = V_{\text{exchange}} + V_{\text{dipole}} - E_F$, where E_F is the energy at the Fermi level. Variations of the work function from crystal face to crystal face are well documented.

Surface irregularities, like atomic height steps at the surface exhibit different work functions as determined by Wagner and Besocke recently.³⁸ Recent theoretical studies provide firm foundation of the effect of surface heterogeneity and irregularities on the density of states at the Fermi level³⁹ and on the angular distribution of charge densities⁴⁰ at these low coordination number surface sites. The structural heterogeneity at the surface leads to the chemical heterogeneity, i.e., the ability of the surface to carry out complex chemical rearrangements involving the simultaneous forming and breaking of surface bonds of varied strength at the various atomic surface sites.

The Surface Crystallography of Adsorbed Monolayers of Atoms

The structural asymmetry and excess charge experienced by atoms at the surface have an important effect on the structure of the adsorbate

substrate system. In the presence of adsorbates, bonds are formed that make optimum use of the available bonding orbitals. For small adsorbed atoms and molecules this often leads to the formation of a close-packed adsorbate structure in which the adsorbate occupies the high symmetry atomic sites that correspond to the continuation of the bulk structure. We shall review several examples of chemisorbed structures of these types below.

For most of the over 200 surface structures of adsorbed monolayers that have been studied so far, only the two-dimensional symmetry of the diffraction pattern has been determined.⁴¹ Thus, only the size and shape of the two-dimensional surface unit cell is known. Determination of the actual positions of the adsorbed atoms requires analysis of the intensity of the diffraction beam and has been performed only on a small number of systems, almost all for atomic adsorption and low Miller Index surfaces of face-centered cubic metals. The first of these analyses was carried out by Anderson and Pendry,⁴² who examined sodium adsorption on the nickel (100) crystal face and reported that the sodium atoms occupy four-coordinated sites at a distance of $0.87 \text{ \AA}$ above the top-most nickel layer. Demuth et al.⁴³ have examined the overlayer structures of oxygen, sulfur, selenium and tellurium on nickel (100). On this surface they find the adsorbed atom to occupy four-coordinated bonding sites at displacements of 0.9, 1.3, 1.45 and $1.9 \text{ \AA}$ respectively from the center of the top nickel layer. Results are also given for nickel (111) and nickel (110). Forstmann et al.⁴⁴ reported iodine adsorbed on Ag(111) to occupy the three-fold sites at a distance of $2.5 \text{ \AA}$ above the top-most layer. Oxygen adsorption on tungsten⁴⁵ and nitrogen on tungsten⁴⁶ and other body-centered cubic metals have also

been studied.

Several general observations appear to be emerging from this work. Chemisorbed atoms seek an adsorption site which allows them to maximize their coordination. The substrate-adsorbate bond length, at least for the strongly chemisorbed systems studied thus far, can be reproduced rather well by adding the metallic radius of the substrate and the single bond covalent radius of the adsorbate. This is shown in Table II which lists the experimentally determined bond length and the predicted bond length obtained by summing the covalent radii. In most cases, the difference is within the $0.1 \text{ \AA}$ accuracy claimed for the experimental determination and in no case is the discrepancy greater than ten percent. This result suggests that the chemisorption bond of the small adsorbate atoms studied so far is basically covalent in character, which means that theoretical treatment in terms of localized surface complexes and clusters should be applicable to their chemisorption.

The small adsorbate atoms that are listed in Table II occupy sites of the highest symmetry. These sites would also be the location of the next layer of metal atoms if we were to continue building up the solid layer by layer. The adsorbate-metal atom bond distance is equal, within the experimental accuracy, to the sum of the covalent radii of the two atoms. There are other types of surface bonding, however, that are neither simple nor readily rationalized using simple chemical arguments. For example, when oxygen adsorbs on nickel (110), the best agreement with experiment is obtained assuming that oxygen atoms are lying in a two-fold bridge site between 1.41 and $1.51 \text{ \AA}$ above the nickel layer.⁴⁷ This is clearly not the highest coordination site on the surface. The fact that bridge

bonding is preferred suggests that atomic oxygen bonds to two adjacent nickel atoms via the oxygen p_x and p_y atomic orbitals. The bond angles and atomic distances are very close to what one expects from X_2O compounds, where X is the metal atom.

Another example of unusual bonding is detected in studies of hydrogen adsorption to the nickel (110) surface recently. A new surface structure forms and surface crystallography studies indicated that this unit cell is a consequence of the restructuring of the nickel (110) surface as a result of hydrogen chemisorption and not due to ordering of the hydrogen adsorbate.⁴⁸ The surface structure model that gave best fit to the experimental data consists of distorting the nickel surface atoms so as to produce the new (1x2) periodicity. This is carried out by simple depression or raising of every alternate row of nickel atoms in one direction, or a pair-wise distortion of every alternate row of nickel atoms in the plane of the surface. The optimal agreement with experimental curves is obtained by a 0.1 Å compression of the surface layer and a 0.1 Å alternate displacement of the rows of nickel atoms in the $[\bar{1}\bar{1}0]$ direction.

Another example of unusual structure comes from studies of the titanium-oxygen system. It has been reported recently⁴⁹ that upon chemisorption, oxygen atoms are located below the first layer of titanium atoms in the (0001) surface. There is little doubt that future studies will reveal the richness and complexity of surface bonding and will yield many unexpected bonding configurations.

Studies of Hydrocarbon Bonding to Metal Surfaces

A. The Surface Crystallography of Acetylene on Pt(111)

Acetylene, C_2H_2 , forms a (2x2) overlayer on the platinum (111) crystal

surface. In recent experimental studies, Stair and Somorjai and Kesmodel et al. have reported the LEED I-V profiles for the acetylene-platinum system.^{50,51} In particular, two different (2x2) structures of adsorbed acetylene were identified, which we refer to briefly as stable and metastable state and which have been interpreted as involving different chemical bonding. The metastable (2x2) structure is observed to form initially at low exposure (one Langmuir = 10^{-6} torr-sec) of C_2H_2 at room temperature but transforms in one hour to the stable (2x2) structure upon gentle heating to 100°C. Both structures are characterized by the same (2x2) surface unit cell and involve the same carbon coverage as determined by Auger electron spectroscopic analysis. However, they are readily distinguishable by their different I-V characteristics.

Let us examine the various modes of bonding of acetylene to platinum in the context of high symmetry bonding sites available on the (111) face of an f.c.c. crystal. As illustrated in Fig. 5, we distinguish four sites designated as: a) one-coordinate π ; b) di- σ and c) bridging (sometimes referred to as μ -bridging) and d) triangular complexes. We have indicated for each site only those surface metal atoms expected to have significant metal-carbon interaction. It is natural to discuss these surface geometries in terms of structural analogies of organo-metallic complexes. In these terms, the one-coordinate π complex, a), involves the interaction of one or both sets of π orbitals of the acetylene molecule with a single metal surface atom. The bridging site, c), utilizes both sets of π orbitals to bond with two surface atoms; both a) and c) in principle entail little rehybridization of the molecule since essentially undistorted π orbitals would be involved. However, the di- σ bond, b),

implies $sp+sp^2$ rehybridization and the formation of two carbon metal σ bonds accompanied by large hydrogen cis bending (CCH angle $\approx 120^\circ$). This possibility has received serious consideration in the catalysis literature. Finally, the triangular structure, d), commonly found in tri-nuclear metal alkyne complexes illustrates a mode of bonding loosely referred to in terms of both σ and μ bonds. This triangular geometry is found to be the favored arrangement in the stable structure. Analysis of Figs. 6 and 7 and other data similarly obtained shows that the triangular geometry gives consistently better agreement than either the bridging or di- σ geometries. The one-coordinate π complex can be ruled out readily as well. For a z-distance of 1.9 Å C-Pt distances of 2.2 Å are found for C_2H_2 centered on the triangular site. This value is very close to the predicted covalent bond distance of 2.16 Å.

It has been possible to distinguish amongst various proposed bonding models for acetylene adsorption on the Pt(111) surface using dynamical analysis of low-energy electron diffraction intensity profiles. It was found that bonding of acetylene in a triangular site on the Pt(111) surface is the stable and preferred configuration. It is interesting to note that this same bonding geometry is exhibited in tri-nuclear metal alkyne clusters; moreover, the average C-Pt distance found for C_2H_2 adsorbed on Pt(111) is similar to that determined for the osmium tri-nuclear cluster, the osmium covalent radius being only 0.04 Å shorter than that of platinum. Although one cannot detect a small C-C bond length change we do anticipate a C-C bond stretch of about 0.1 Å to occur for acetylene adsorption judging from the C-C length found in X-ray crystal structure determinations of the metal alkyne clusters.

B. Studies of Other Hydrocarbons by Electron Spectroscopy

The bonding and the composition of C_2H_4 was studied on the nickel (111) crystal face by (UPS).⁵² At 100 K, the organic molecule adsorbs by bonding via its π orbitals to the metal surface. On heating to 230 K, C_2H_4 dehydrogenates to form C_2H_2 that is bound with even stronger π bonds to nickel surface. UPS could monitor changes in bonding caused by the activated dehydrogenation that occurs as a function of temperature. Chemisorption involved predominantly π -d bonding, thus rehybridization of the adsorbed molecule does not seem to occur.

Similar studies were carried out with C_2H_4 adsorbed on the W(110) crystal face.⁵³ At 300 K, the molecule dehydrogenates upon adsorption to form C_2H_2 that π bonds to the metal. As the surface temperature is increased to 500 K, breaking of the carbon-hydrogen bond occurs and the C_2 fragments are identified by UPS by the presence of C-C and C-W bonds. Upon heating to 1100 K, the C-C bond breaks and carbon atoms remain on the surface in a disordered state.

One of the striking features of the adsorption process is the existence of small (of the order of kT) activation energy barriers in the path of various bond breaking reactions. As a result an organic molecule may be adsorbed intact even on the most reactive metal surface at sufficiently low surface temperatures. As the temperature is increased, electron spectroscopy can be used to identify the different bond breaking processes that seem to occur in readily distinguishable steps.

Studies of CO Bonding

The chemisorption of CO was studied on several metal surfaces by electron spectroscopy. Using synchrotron radiation, Shirley et al. have

found that CO adsorbed in a bridge structure bound through the carbon to the metal on the platinum (111) crystal face, while the oxygen end of the molecule is pointing away from the surface.⁵⁴ Using the high Miller Index (775) surface that has a large concentration of kink atoms of low coordination number, Mason *et al.* found that the CO dissociates at the kink sites,⁵⁵ while the carbon monoxide does not dissociate on atoms in terrace sites. These studies were carried out using UPS and XPS techniques. The concentration of carbidic carbon was equal to the kink concentration and was produced at the initial stages of CO chemisorption on this kinked, high Miller Index platinum surface. Thus, the adsorption of CO takes place first at kink sites where the molecule dissociates. Once the kinks are blocked by carbon, CO further chemisorbed in the molecular state on the other atomic sites of the heterogeneous platinum surface. CO adsorbed in several bonding sites, some of them molecular, some of them dissociated on tungsten crystal surfaces.⁵⁶

The Surface Composition of Binary Alloys

The composition of alloys in the topmost monolayer is likely to be very different from the bulk composition for several reasons and we shall review briefly each one of them.

a) For systems that exhibit regular solution behavior, the surface free energy (which is always positive) is minimized by the segregation of that constituent with the lower surface tension. For metals that have high tensions as compared to organic surfaces or most oxide surfaces, such surface enrichment is likely to be very marked indeed. For a system obeying regular solution theory, it has been shown^{57,58} that the composition of the surface monolayer is given by Eq. (1).

$$\frac{x_1^A}{x_1^B} = \frac{x_b^A}{x_b^B} \exp \left(\frac{(\sigma^B - \sigma^A)a}{RT} \right) \exp \left[\frac{\Omega(\ell+m)}{RT} \left((x_b^B)^2 - (x_b^A)^2 \right) + \frac{\Omega\ell}{RT} \left((x_1^A)^2 - (x_1^B)^2 \right) \right] \quad (1)$$

Where x_1 and x_b are the atom fractions in the surface monolayer and bulk, respectively. In this expression σ is the surface energy, a is the molar surface area, T is the absolute temperature, R is the ideal gas constant, Ω is the regular solution parameter which is given from the heat of mixing ΔH_m by

$$\Omega = \Delta H_m / x_b^B x_b^A \quad (2)$$

The packing parameter ℓ gives the fraction of an atom's nearest neighbors which are in the same plane parallel to the surface as the atom. Similarly m is the fraction of nearest neighbors which are in an adjacent parallel plane. For instance, in an fcc lattice, an atom has 12 nearest neighbors so a (111) plane has 6 nearest neighbors in the plane of an atom and 3 nearest neighbors in the plane below the atom. Thus in this case $\ell = 6/12$ and $m = 3/12$.

Electron spectroscopy techniques, especially Auger electron spectroscopy and photoelectron spectroscopy, have been eminently successful in determining the surface phase diagrams, i.e., the surface composition as a function of bulk composition and temperature, for several binary metal systems. A typical Auger spectrum of an alloy system that of palladium-gold is shown in Fig. 8.⁵⁹ From the Auger peak intensities one may determine surface composition for a series of bulk compositions and from this data the surface phase diagram is deduced. The most serious experimental difficulty in converting the Auger peak intensities to surface concentrations lies in estimating the depth near the surface from which the Auger electrons

of different kinetic energy are emitted and the relative scattering power of the two types of atoms in this volume sampled by the electrons. Since part of the Auger signal is due to atoms below the surface, it is essential to subtract this part from the signal intensities in order to extract the surface contribution. Much of the discrepancy between results reported from different laboratories on the same alloy system can be attributed to difficulties in estimating relative contributions of surface atoms to the various Auger peak intensities.

b) Adsorbed gases or impurities segregating at the surface can markedly change the surface composition. If one of the constituents forms strong chemical bonds with the adsorbate (oxygen, CO, carbon, sulfur or calcium, most commonly) it will be accumulating on the surface even though that it may not be at the surface in the absence of the adsorbate. CO, for example, that forms strong bonds with many transition metal atoms may aid the segregation of these atoms at the surface at the expense of other constituents that form weak CO bonds. In essence an adsorbate converts a two-component system to a three component system thereby altering the surface composition at equilibrium.

c) Solute atoms with large or small radii with respect to the size of the solvent (majority) atoms may be "excluded" from the bulk because they introduce excessive strain in the crystal lattice. As a result, surface segregation of one component that is misfit in the crystal lattice can be observed. The strain energy contribution may enhance the surface concentration of that component that would segregate on the surface on account of its effect of decreasing the total surface free energy. Conversely this strain energy contribution may oppose the effect of surface

segregation of one constituent in some cases.

d) There are complex phase diagrams that exhibit the formation of stable compounds of high lattice energy. In this circumstance the energy necessary to exchange the two atoms, A and B, by removing them from their equilibrium lattice site is so large that it overrides the influence of surface forces that would induce surface segregation. Thus the bulk composition pins the surface composition, i.e., the surface and bulk compositions remain identical. We have found in studying the complex gold-tin phase diagram that this phenomenon occurs at the bulk composition of AuSn that forms a compound with high cohesive energy.

In Table III we list those metal systems that have been studied by electron spectroscopy and indicate which element is found in excess at the surface. The surface composition is determined by the interplay of three physical parameters: 1) the surface free energy difference of the two components, 2) the relative sizes of the two types of atoms in the alloy and 3) the magnitude of the bond energy between unlike atoms when a compound forms. For regular solutions 1) and 2) determine the surface composition. For substitutionally ordered compounds of high binding energy 3) may override the effects of 1) and 2).

Studies of Catalytic Reactions

The purpose of these investigations is to understand the mechanism of catalyzed surface reactions on the atomic scale. We have recently developed new instruments for in situ studies of the reactivity of crystal surfaces at both low and high pressures. The scheme of one of these apparatus is shown in Fig. 2. At low pressures (10^{-7} - 10^{-4} torr), the reaction rate and product distributions are monitored by a quadrupole mass

spectrometer while the surface structure and composition are determined by low-energy electron diffraction and Auger electron spectroscopy, respectively. Then a small cup (total volume approximately 10 cm^3) can be placed around the crystal sample that isolates it from the rest of the chamber that can be pressurized to over 100 atmospheres, if desired, using the mixture of gaseous reactants. The high pressure reaction chamber is connected to a gas chromatograph that serves to monitor both rate and product distributions in this circumstance. The structure and composition can be determined in situ by LEED and Auger before and after the high pressure experiment once the cup is removed.

Catalysis of Hydrocarbon Reactions by Platinum

Dehydrogenation of cyclohexane or cyclohexene to benzene occurs only on stepped platinum surfaces at an appreciable rate at low pressures. Fig. 9 shows the step and kink density dependence of the rate of cyclohexene dehydrogenation to benzene to demonstrate this effect. While the rate increases markedly with increasing step density (Fig. 9a), it is relatively unaffected by changes of kink density (Fig. 9b).

The rate of cyclohexane dehydrogenation to benzene is constant as long as there are steps on the catalyst surface, but it is almost an order of magnitude lower on the Pt(111) surface, as seen in Fig. 10a. Thus atomic steps appear to be preferred surface sites for breaking H-H and C-H bonds (H-H bond breaking has been studied by the $\text{H}_2\text{-D}_2$ exchange).

Cyclohexane undergoes both dehydrogenation and hydrogenolysis on the stepped Pt surfaces. The relative rates of these two reactions can best be monitored by the ratio of benzene to n-hexane in the reaction product. As is demonstrated in Fig. 10, the rate of benzene production is independent

of step and kink density while n-hexane production increases slowly with step and kink density and rapidly with kink density. Rates of cyclohexane hydrogenolysis to n-hexane per kink site is determined by the slope of the line in Fig. 7b representing hydrogenolysis and is 3×10^{28} moles of n-hexane/kink atom/sec. This is almost an order of magnitude higher than the slope in Fig. 8a which is 4×10^{-29} moles of n-hexane/step atom/sec. The observed low hydrogenolysis activity on the type of stepped surfaces represented by Fig. 10a may be caused by some thermally regenerated kinks in the steps. n-Hexane formation and the formation of other hydrogenolysis products must be the result of C-C bond scissions. It appears that kinks are very effective in breaking C-C bonds in addition to C-H and H-H bonds. Thus we have been able to identify two active sites of lower coordination number of platinum surfaces: steps with C-H and H-H and kinks in steps with C-C, C-H and H-H bond breaking activity.

The Hydrogenation of CO and CO₂ Over Polycrystalline Rhodium at One Atmosphere¹⁴

The formation of hydrocarbons from CO-H₂ mixtures is thermodynamically favorable, although higher pressures (in excess of one atmosphere) are necessary to facilitate the formation of higher molecular weight products.

The rates of formation of products by this reaction are very low as compared to other hydrocarbon reactions (dehydrogenation or hydrogenolysis). Thermodynamic equilibrium between reactants and the many possible products is not established even at the high pressures commonly employed.

We have studied the reaction of CO and H₂, and CO₂ and H₂ to form hydrocarbons, using polycrystalline rhodium as a catalyst. The kinetics

of methanation on this metal foil of about $\sim 1 \text{ cm}^2$ area, is in excellent agreement with the results obtained on dispersed and supported rhodium catalysts.

There is evidence for the presence of both molecular and dissociated CO on the surface, during the synthesis. The active rhodium surface develops a carbonaceous deposit, whilst chemisorbed oxygen is rapidly removed from the surface layer by CO and H_2 . Oxygen also appears to be located below the metal surface. By changing the composition and/or structure of the rhodium-carbon surface complex by pretreatment (with acetylene or oxygen) both the reaction rate and the product distribution can be markedly altered. The $\text{CO}_2\text{-H}_2$ reaction yielded methane predominantly in contrast with the much broader distribution obtained from CO-H_2 reactions under the same conditions.

Variation of methanation activity and product distribution on clean and pretreated rhodium surfaces is shown in Table IV.

The high pressure apparatus has been a great asset to correlate the reactivity of the surface with the catalyst surface structure and composition for the important CO-H_2 and $\text{CO}_2\text{-H}_2$ reactions. As a result a better physical picture of heterogeneous catalysis emerges. It is my hope that using similar apparatus the reactivity, the structure and the composition at solid-liquid interfaces will also be explored.

Correlations of Structure, Composition and Reactivity at Solid-Gas and Solid-Liquid Interfaces

The same questions that are asked in studies of solid-gas interfaces are also important to answer in studies of solid-liquid interface phenomena. What is the atomic and electronic structure and composition of the

solid surface at the liquid interface in the presence of an external electric field and in the absence of such an electrochemical potential? How does this structure and composition correlate with reactivity during an electrochemical reaction or for surface reactions at the liquid interface? Since the solid surface structure and composition cannot be studied in the presence of a liquid with our surface-sensitive techniques that are presently available, just as in the case of high pressure, solid gas studies, the surface structure and composition will have to be determined before and after the solid-liquid interface reaction.

The simplest question that one may ask is whether the stable surface structure of adsorbates and the bonding of these adsorbates are the same when adsorption occurs from the liquid face as compared to that from the vapor of the same molecule. Water or organic solvents (n-heptane, benzene, etc.) and ionic substances (sulfates, chlorates, halogens and alkali metals) may come to mind as likely candidates for these studies. The high pressure apparatus that has been described above is most suitable to carry out these investigations. One may wish to investigate the surface structure of a single crystal face as the external electrochemical potential is changed. Simultaneously, one would wish to determine how the surface composition varies as oxidation or reducing surface conditions are established using an external potential. For example, what is the coverage and bonding of oxygen and hydrogen on the surface as a function of variation of the external electric field. The aim of these early studies should be to discover patterns of similarity and change with studies of the same type at the solid-liquid and solid-gas interface. Once these correlations of changes of surface structure and composition are established,

electrochemical and other solid-liquid interface studies can draw on the wealth of information that is available from studies of the solid-gas interface. Then patterns of similarity may emerge for surface reaction studies as well, such as electrocatalysis and heterogeneous catalysis.

Admittedly, during the transient period while the liquid phase or high pressure gas phase are removed from the vicinity of the solid surface to be studied, many of the weakly bound surface intermediates may change their bonding to desorb altogether. Thus, studies of the surface structure and composition before and after the surface reaction may not always yield a complete physical picture of the working surface under reaction conditions. It is feasible, however, to remove or reintroduce a liquid or high pressure gas within milliseconds thereby increasing the probability to detect even weakly bound, short residence time surface species. (The surface residence time (τ) is commonly given as $\tau = \tau_0 \exp(\Delta H/RT)$ where τ_0 is often equated with vibrational times approximately 10^{-12} seconds and ΔH is the heat of adsorption.) Such rapid pumping techniques will be developed in the near future no doubt.

Modern surface science developed on account of the atomic and molecular level information that has become available by applications of the new surface diagnostic techniques. Determination of the structure and composition of the working metal catalyst or the corroding surface presented also the opportunity to develop new catalysts and to passivate the surface against corrosion. There are several innovations of commercial significance that owe their birth to modern surface science. It is likely that studies of the solid-liquid interface will yield major advances in the field of electrochemistry and perhaps establish new areas

of electrochemical science.

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Figure Captions

- Fig. 1. Diffraction pattern and schematic of mean surface configurations for platinum crystal surfaces exhibiting a) low defect density, b) regular step arrays with an average spacing between steps of 6 atoms and c) regular step arrays with kink sites along the steps. Note the spot splittings in b) and c) indicative of the periodic step arrays.
- Fig. 2. Surface analysis apparatus for catalytic studies and for studies of the solid-liquid interface at high pressures (0.1-100 atm) with a small volume isolation cell.
- Fig. 3. a) Diffraction pattern from the Pt(100)-(5x1) structure. b) Schematic representation of the (100) surface with hexagonal overlayer. c) Diffraction pattern from the Pt(100)-(1x1) structure. d) Schematic representation of the (100) surface.
- Fig. 4. Model of heterogeneous solid surface depicting different surface sites. These sites are distinguishable by their number of nearest neighbors.
- Fig. 5. Schematic indicating various high symmetry local bonding sites for acetylene on the (111) face of an f.c.c. crystal: a) one-coordinate π , b) di- σ , c) bridging and d) triangular.
- Fig. 6. Comparison of calculated I-V profiles for various model geometries ($\tau = 1.9 \text{ \AA}$) to experiment (stable acetylene overlayer) for two fractional order beams.
- Fig. 7. Comparison of calculated I-V profiles for various model geometries ($\tau = 1.9 \text{ \AA}$) to experiment (stable acetylene overlayer) for two integral-order beams.

Fig. 8 Derivative Auger spectra for pure gold, pure tin and two representational alloys.

Fig. 9 Initial rate of cyclohexene dehydrogenation to benzene on platinum single crystal catalysts as a function of a) increasing step density and b) increasing kink density at constant step density. The reaction conditions are 5×10^{-8} torr of cyclohexene, 1.0×10^{-6} torr of hydrogen and 423 K catalyst temperature.

Fig. 10 Initial steady-state rates of cyclohexene dehydrogenation to benzene (o) and hydrogenolysis to n-hexane (Δ) on platinum single crystal catalysts as a function of a) increasing step density and b) increasing kink density at constant step density of 2.4×10^{14} step atoms/cm². The reaction conditions are 5×10^{-8} torr of cyclohexene, 1.0×10^{-6} torr of hydrogen and 423 K catalyst temperature. The rate of dehydrogenation is constant at 2.8×10^{-14} mol cm⁻² s⁻¹ with steps present but is less (0.3×10^{-14} mol cm⁻² s⁻¹) on the (111) surface (near zero step density). The rates of hydrogenolysis per surface sites are the slope of the lines representing hydrogenolysis and are 3×10^{-28} mol (kink atom)⁻¹ s⁻¹ and 4×10^{-29} mol (step atom)⁻¹ s⁻¹.

Table I Techniques of surface analysis that are most frequently employed at present.

Technique	Probe	Main Output Information	Sensitivity (Monolayer)	Depth Sampled	Commercially Available	Depth Profile
A E S Auger Electron Spectroscopy	Electrons ~2 KeV ~50 μ A	Surface Composition Qualitative & Quantitative	$\sim 10^{-2} - 10^{-3}$	1 - 7 Layers	YES	YES
L E E D Low Energy Electron Spectroscopy	Electrons ~100 eV ~10 μ A	Surface Structure	$\sim 10^{-1} - 10^{-2}$	1 - 7 Layers	YES	NO
X P S X-Ray Photoelectron Spectroscopy	X-Rays ~1 KeV	Oxidation State & Composition	$\sim 10^{-1} - 10^{-2}$	1 - 7 Layers	YES	YES
I S S Ion Scattering Spectroscopy	Ions He, Ne ~1 KeV ~ 10^{-3} A	Surface Composition	$\sim 10^{-3} - 10^{-4}$	1 Layer	YES	YES
S I M S Secondary Ion-Mass Spectroscopy	Ions Ne, Ar, O ₂ ~1 KeV ~ 10^{-3} A	Surface Composition	$\sim 10^{-6}$	1 Layer	YES	YES

Table II

Adsorbate-Substrate Bond Lengths Determined by LEED

Substrate	Adsorbate	Bond Length (experimental)	Bond Length (predicted)
Ni(001)	O	1.97 Å	1.90 Å
	S	2.18 Å	2.28 Å
	Se	2.27 Å	2.41 Å
	Te	2.58 Å	2.61 Å
	Na	3.37 Å	3.10 Å
Ni(110)	O	1.91 Å	1.90 Å
	S	2.17 Å	2.28 Å
Ni(111)	S	2.02 Å	2.28 Å
Ag(001)	Se	2.80 Å	2.61 Å
Ag(111)	I	2.75 Å	2.77 Å
Al (100)	Na	3.52 Å	3.32 Å
Mo(001)	N	2.02 Å	2.03 Å
W(110)	O	2.08 Å	2.05 Å

Table III

Surface Enrichment of Binary Metal Alloys

<u>System</u>	<u>Object</u>
Ag-Au ⁽²⁸⁾	Ag
Ag-Pd ⁽³¹⁾	Ag
Al-Cu ⁽³²⁾	Al
Au-Cu ⁽³³⁾	Au
Au-In ⁽³⁴⁾	In
Au-Ni ⁽³⁵⁾	Au
Cu-Ni ^(36,37)	Cu
In-Pb ⁽³⁸⁾	Pb
Ni-Pd ⁽³⁹⁾	Pd
Fe-Cr ⁽⁴⁰⁾	Cr
Pt-Sn ⁽⁴¹⁾	Sn

Table IV Variation in methanation activity, and product distributions for the CO-H_2 and $\text{CO}_2\text{-H}_2$ reactions on clean and pretreated rhodium surfaces. (Reaction conditions 1:3 ratio, 700 Torr, 300°C)

Reaction Gases	Surface [*] Pretreatment	Methanation Rate (300°C) (turnover number)	Product Distribution
CO-H_2	none	$0.15 \pm .05$	88% C_1 9% C_2 3% C_3
$\text{CO}_2\text{-H}_2$	none	$0.33 \pm .05$	100% C_1
CO-H_2	O_2	$0.33 \pm .05$	87% C_1 10% C_2 3% C_3
$\text{CO}_2\text{-H}_2$	O_2	1.7 ± 0.2	98% C_1 2% C_2
CO-H_2	CO	$0.15 \pm .05$	88% C_1 9% C_2 3% C_3
$\text{CO}_2\text{-H}_2$	CO	$0.33 \pm .05$	100% C_1
CO-H_2	C_2H_2	$.07 \pm .02$	78% C_1 18% C_2 4% C_3
$\text{CO}_2\text{-H}_2$	C_2H_2	$.07 \pm .04$	96% C_1 3% C_2 1% C_3

* Heated for 15 mins in 700 Torr of the particular gas, then thermally desorbed to 1000°C in vacuo before reaction.

a) Pt - ($\bar{1}11$)

b) Pt - ($\bar{5}57$)

c) Pt - ($\bar{6}79$)

XBB 7111-5903

Fig. 1

XBL763-6613

Fig. 2

XBB 7111-5356

Fig. 3

XBL 708-1717 A

-41-

(a)

(b)

(c)

(d)

XBL 767-7141

Acetylene on Pt (III)
Stable Structure

xBL 767-7145

XBL 767-7146

XBL 765-6817

XBL756-3164A

XBL 756-3163 A

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