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THE MOLECULAR SURFACE SCIENCE OF HETEROGENEOUS CATALYSIS. HISTORY AND PERSPECTIVE

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August 1983

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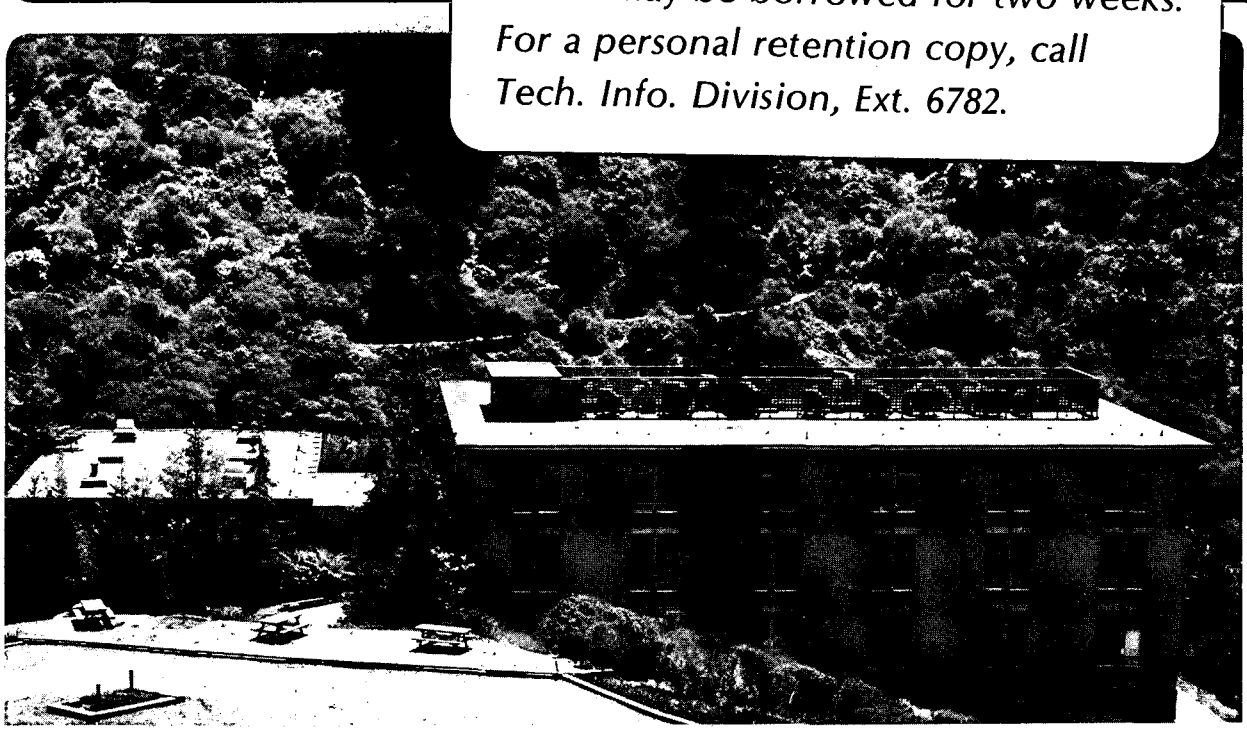

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THE MOLECULAR SURFACE SCIENCE OF HETEROGENEOUS CATALYSIS. HISTORY AND PERSPECTIVE

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It is a rare occasion that a lecture invitation permits in fact, requests a personal and historical review and discussion of ones research. I am grateful for this opportunity and shall attempt to describe how I became involved with modern surface science and how it was employed in my laboratory for studies of the chemistry of surfaces and heterogeneous catalysis. Out of this research came new approaches that have impact on catalysis science and technology.

In 1957, when I entered graduate school in Berkeley in chemistry, having just arrived from Hungary, there were two fields of chemistry, heterogeneous catalysis and polymer sciences that caught my imagination and I wanted to pursue. None of the faculty members at Berkeley were carrying out research in these areas. Nevertheless, Richard Powell, an inorganic chemist and kineticist, was willing to give me a research project in catalysis. As a result my Ph.D. research explored changes of particle size and shape of dispersed platinum catalysts supported on γ alumina when subjected to oxidizing and reducing atmospheres. The technique I used for these studies was small angle X-ray scattering.[1] During the three years it took me to finish the project, I learned a great deal about catalysis, and I also learned that important advances in our understanding in physical chemistry can only be made if techniques are available for the molecular level scrutiny of catalysts. It was not too difficult to see that only those fields entered the mainstream of research of modern

physical chemistry that permitted molecular level studies via spectroscopy or diffraction. When I finished my Ph.D. research in 1960, surface chemistry and catalysis were not among these fields. With the exception of Field Emission and Field Iron Microscopies, there were no techniques available for atomic scale studies of surfaces that could be broadly employed. So I left the field and carried out solid state chemistry and physics research at IBM in New York for the next four years, concentrating on studies of the vaporization mechanisms of single crystals of cadmium sulfide and other II-VI compounds.

In the meantime, low energy electron diffraction (LEED), made its appearance as a practical tool to detect the structure of ordered surfaces and adsorbed monolayers as a result of innovations in instrumentations by Germer in the Bell Laboratories. I was instantly fascinated with the opportunities this technique presented for the definitive atomic level studies of surface structure and the ability to obtain clean surfaces of single crystals when coupled with ultra-high vacuum and sputter etching that was developed a few years before by Farnsworth. Upon moving to Berkeley in 1964 as an Assistant Professor, I started LEED studies on platinum (Pt) single crystal surfaces in the hope that one of these days we shall learn what is so unique about the platinum surfaces that makes this metal such an excellent catalyst for hydrocarbon conversion reactions, especially for dehyrocyclization of aliphatic molecules to aromatic species. In early 1965, our first (100) Pt single crystal surfaces exhibited strange diffraction patterns which led us to the discovery of surface reconstruction[2]

of metal surfaces (Figure 1). While semiconductor surfaces were known by that time to have surface structures that are different from that expected from the surface projection of the bulk unit cell, this was the first time a metal has shown similar features. Shortly thereafter, the iridium (100)[3] and the gold (100) surfaces[4] were reported to exhibit similar reconstructed surface structures. It took fifteen years which was needed for the development of the theory of low energy electron diffraction and surface crystallography to solve this structure,[5] which we did in 1980 (Figure 2). The square unit cell of the Pt(100) surface is buckled into an hexagonal arrangement. The periodic coincidence of atoms in the hexagonal layer with atoms in the underlying square layer produces the busy diffraction pattern and complex unit cell that is shown in Figure 1.

The next seven years saw an explosive development of new techniques to study the properties of the surface monolayers. Auger electron spectroscopy (AES) was developed by Harris and others to determine the surface composition and X-ray photoelectron spectroscopy (XPS) was developed to identify the oxidation states of surface atoms. These three techniques, LEED, AES and XPS contributed the most of all other techniques available to the unraveling of the molecular properties of the surface monolayer.[6,7] Simultaneously experimental studies were busily coming up with new surprising surface properties, mostly of low Miller Index flat surfaces. Among these properties, perhaps the most striking were: (1) the prevalence of ordering of clean surfaces and of adsorbed layers of atoms and molecules.[8] Hundreds of ordered monolayer surface structures were discovered that undergo

alterations as a function of temperature and coverage. Surface phases with order-order and order-disorder transformations were uncovered that yield complex adsorption isotherms where the relative strength of adsorbate-substrate and adsorbate-adsorbate interactions control the structural changes. Good examples of these are the surface structures that form on adsorption of CO on Rh(111)[9] and other transition metal surfaces, O on Rh(111) surfaces[10] and sulfur on the molybdenum (100) surface;[11] (2) reconstruction and relaxation of clean surfaces is more of a rule than an exception. Surface structure analysis by LEED surface crystallography indicates that the surface atoms in many solid surfaces seek new equilibrium positions as a result of the anizotropy of the surface environment.[6] This of course leads to surface reconstruction. An equally common observation is relaxation where the interlayer distance between the first and second atomic layers are shorter than the interlayer distances in subsequent layers below the surface. Surface relaxation can be readily rationalized if one assumes the surface atoms to be intermediate between a diatomic molecule and atoms in a bulk surrounded by many neighbors. The interatomic distances in diatomic molecules are much shorter than the interatomic distances in the bulk solid. Thus, such a contraction between the first and second layers of atoms at the surface is just what one expects, based on such a simple model. It is also found, in agreement with the predictions of this model that the more open the surface the larger the contraction between the first and second layer; (3) The surface composition of multicomponent systems (alloys, oxides, etc.) is different from the bulk composition.[12,13] There is surface segregation of one of the constituents that lowers the surface free energy of the multicomponent

system. The contamination of most surfaces with carbon, sulfur, silicon-dioxide and other impurities can be explained as due to the surface thermodynamic driving force that is behind surface segregation. The thermodynamics of surface segregation was developed and good agreement between experiments and calculated surface compositions has been obtained for many binary alloy systems.[14] In Table 1, several binary metallic systems are listed for which there is surface segregation of one of the constituents. For a two component system that behaves as an ideal or as a regular solution, the atom fractions at the surface can be related to the atom fractions in the bulk as shown in Figure 3. We can also predict how the changed surface composition in the surface monolayer is modified layer by layer as the bulk composition is approached. This is shown for the gold silver alloy that forms a regular solid solution in Figure 4. The first surface layer is rich in silver,[15] the second layer is rich in gold, the third layer is again rich in silver, and by the fourth layer the bulk alloy composition is reestablished. We can actually see the beginning of compound formation by the alternation of excess constituents for alloys with exothermic heat of mixing, layer by layer.

It is often found that the oxidation states of the surface atoms are often different than for atoms in the bulk. Aluminum oxide and vanadium pentoxide[16,17] are two examples where definitive experimental surface science studies indicated reduced oxidation state for the metal ions in the surface layers.

The techniques of LEED, AES, XPS were static techniques. There was a need to develop dynamic measurements to study the kinetics of surface processes and we developed molecular beam surface scattering[18].

The scheme of the molecular beam surface scattering experiment is shown in Figure 5. This is one of the most rapidly developing areas of surface chemical physics today. It can determine the energy states of molecules before and after scattering, or after a reaction at the surface when combined with laser spectroscopy.[19]

Most surface studies, including the adsorption of organic molecules of ever increasing size, were carried out on low Miller Index single crystal surfaces of metals or semiconductors. For example, phtalocyanine adsorbs on the copper (111) surface and forms an ordered layer[20] that can be readily studied by surface science techniques. However, these surfaces are quite inert when viewed from the chemical and especially catalytic points of view. They were unreactive with many reactive molecules at around 300K and at low pressures of 10^{-8} to 10^{-6} torr. Even molecular beam studies using mixed H_2 and D_2 beams failed to detect significant H_2/D_2 exchange on the platinum (111) surface at low pressures. Anyone working in the field of catalysis would know that this reaction at atmospheric pressures occurs readily on any dispersed transition metal surface way below 300K. The reason for the lack of reactivity could be the surface structure or the low pressure conditions or both. So we did two things. We have started studies of high Miller Index surfaces and developed the high-pressure low-pressure apparatus for combined surface science and catalytic studies.

By cutting flat low Miller Index orientation single crystals at some angle with respect to the low index orientation, high Miller Index surfaces were obtained.[21] These surfaces exhibit ordered step terrace arrangements

where the terraces are of variable width, depending on the angle of cut, and they are separated by periodic steps of one atom in height usually (Figure 6). The step periodicity as well the step height can readily be determined by LEED studies.[22] These surfaces can be cut in such a manner that the steps also have a large concentration of kinks (Figure 7). Surfaces may have as much as 40% of their atoms in step sites, and the kink concentration can reach 10%. As compared to these high concentrations of line defects, point defects, such as ad-atoms or vacancies have very small concentrations (less than 1%) when in equilibrium with the bulk and with other surface defects. These steps and kinks are stable under the conditions of most catalytic surface reactions. Figure 6 and 7 show some of the stepped and kinked surfaces that were prepared. These surfaces exhibited very different reactivities as compared to the flat surfaces. Adsorption studies of hydrocarbons and carbon monoxide revealed preferential bond breaking at these defect sites. C-H and C-C bond breaking was readily detectable on stepped or kinked platinum surfaces upon adsorption of organic molecules, even at 300K at low pressures.[23] while under the same circumstances the (111) surface was unreactive. Molecular beam studies of H_2/D_2 exchange on stepped surfaces showed 7 to 10 fold higher dissociation probability [24] of the hydrogen molecule than on the flat (111) crystal face (Figure 8).

During the period of 1972-76 the importance of surface defects steps and kinks in surface chemical phenomena in all kinds has become well documented. Of course we were lucky that the stepped surfaces were also ordered and exhibited periodicities that were readily detectable by low energy electron diffraction before adsorption and after adsorption of various atoms and molecules.

To combine ultra-high vacuum surface science and high pressure catalytic studies, the following apparatus was developed in my laboratory (Figure 9). The small area samples, often single crystals or polycrystalline foils, after suitable surface characterization in ultra-high vacuum by LEED, AES and other surface sensitive techniques is enclosed in an isolation cell that can be pressurized with the reactants.[25] The sample is then heated to the reaction temperature and the products that form are analyzed by a gas chromatograph that is connected to the high pressure loop. The high-pressure reactor can be used in batch or in flow modes.[26] The detection sensitivity of the gas chromatograph is high enough that a $1cm^2$ surface area is adequate to monitor the product distribution as long as the turnover rates over the catalysts are greater than 10^{-4} molecules per site per second. Using this high-pressure low-pressure apparatus, we can carry out catalytic reactions under conditions that are virtually identical to those used in the chemical technology. We can then evacuate the high-pressure cell, open it and analyze the surface properties of the working catalyst in ultra-high vacuum using the various techniques of surface science. Then, the isolation cell may be closed again and the high-pressure reaction may be continued and again interrupted for surface analysis in vacuum. Using this apparatus we showed not only that catalytic reactions can readily be investigated using small area single crystal surfaces but that these surfaces can be used as model heterogeneous catalysts.

In short order, this approach was being used in my laboratory to study hydrocarbon conversion reactions on platinum, the hydrogenation of carbon monoxide on rhodium and iron, and for the ammonia synthesis from nitrogen and hydrogen on iron.

We discovered rapidly that the selectivity is structure sensitive during hydrocarbon conversion reactions. In these studies, the use of flat, stepped and kinked single crystal surfaces with variable surface structure were very useful indeed. N-hexane may undergo several different reactions over platinum as shown in Figure 10. For the important aromatization reaction of n-hexane to benzene and n-heptane to toluene we discovered that the hexagonal platinum surface where each surface atom is surrounded by six nearest neighbors is three to seven times more active than the platinum surface with the square unit cell.[27] This is shown in Figure 11. Aromatization reaction rates increase further on stepped and kinked platinum surfaces. Maximum aromatization activity is achieved in stepped surfaces with terraces about five atoms wide with hexagonal orientation as indicated by reaction studies over more than ten different crystal surfaces with varied terrace orientation and step and kink concentrations. The reactivity pattern displayed by platinum crystal surfaces for alkane isomerization reactions is completely different from that for aromatization. Our studies revealed that the maximum rate and selectivity (rate of desired reaction divided by total rate) for butane isomerization reactions are obtained on the flat crystal face with the square unit cell.[28] Isomerization rates for this surface are four to seven times higher than those for the hexagonal surface and are increased only slightly by surface irregularities on the platinum surfaces as shown in Figure 12.

For the undesirable hydrogenolysis reactions that require C-C bond scision, we found that the two flat surfaces with highest atomic density exhibit very similar low reaction rates. However, the distribution of hydrogenolysis products vary sharply over these surfaces. The hydrogenolysis rates increase markedly three to five fold when kinks are present in high concentrations of the platinum surfaces[29] (Figure 12).

Figure 13 compares the rates of ammonia synthesis over the (111), (100) and (110) crystal faces of iron.[30] The (111) crystal face is 420 times as active and the (100) face is 32 times as active as the (110) iron surface. This reaction was studied by several outstanding researchers that include P. Emmett, M. Boudart, and G. Ertl who worked for a long time on the mechanism of the ammonia synthesis. The extreme structure sensitivity of this reaction was predicted by many. However, this data is the first experimental clear demonstration of this structure sensitivity.

We found that the catalytically active surface is covered by a tenacious carbonaceous deposit that stays on the metal surface during many turnovers of the catalytic reactions. In order to determine the surface residence time of this carbonaceous deposit, the platinum surface was dosed with ^{14}C labeled organic molecules under the reaction conditions.[31] Carbon 14 is a β particle and meter and using a particle detector we monitored its surface concentration as a function of time during the catalytic reaction. Using another surface science technique, thermal desorption, we could determine the hydrogen content of the adsorbed organic layer

by detecting the amount of desorbing hydrogen with a mass spectrometer. From these investigations we found that the residence time of the observed carbonaceous layer depends on its hydrogen content, which in turn depends on the reaction temperature as shown in Figure 14. While the amount of deposit does not change much with temperature, its composition does. It becomes much poorer in hydrogen as the reaction temperature is increased. The adsorption reversibility decreases markedly with increasing temperature, as the carbonaceous deposit becomes more hydrogen deficient. As long as the composition is about $C_nH_{1.5n}$ and the temperature below 450K, the organic deposit can be readily removed in hydrogen and the residence time is in the range of the turnover time. As this deposit loses hydrogen with increasing reaction temperatures above 450K, it converts to an irreversibly adsorbed deposit with composition of $C_{2n}H_n$ that can no longer be removed readily (hydrogenated) in the presence of excess hydrogen. Nevertheless, the catalytic reaction proceed readily in the presence of this active carbonaceous deposit. Around 750K, this active carbon layer is converted to a graphitic layer that deactivates the metal surface and all chemical activity for any hydrocarbon reaction ceases. Hydrogen-deuterium exchange studies indicate rapid exchange between the hydrogen atoms in the adsorbed reactive molecules and the hydrogen in the active but irreversibly adsorbed deposit. Only the carbon atoms in this layer do not exchange. Thus one important property of the carbonaceous deposit is its ability to store and exchange hydrogen. The structure of adsorbed hydrocarbons, the fragments that form and changes of their stoichiometry and structure can readily be studied by combined LEED and high resolution electron energy loss (HREELS) techniques.[32] The surface structure determination of

organic monolayers is one of the major directions of research that I pursue in my laboratory and it will be for many years to come.

How is it possible that the hydrocarbon conversion reactions exhibit great sensitivity to surface structure of platinum, while under reaction conditions the metal surface is covered with a near monolayer carbonaceous deposit.[2] In fact, often more than a monolayer amount of carbon containing deposit is present as indicated by surface science measurements. In order to determine how much of the platinum surface is exposed and remains uncovered we utilize the adsorption and subsequent thermal desorption of carbon monoxide. This molecule, while readily adsorbed on the metal surface at 300K and at low pressures, does not adsorb on the carbonaceous deposit. Our results indicated up to 10% to 15% of the surface remains uncovered while the rest of metal surface is covered by the organic deposit.[31] The fraction of uncovered metal sites decreases slowly with increasing reaction temperature. The structure of these uncovered metal island is not very different from the structure of the initially clean metal surface during some of the organic reactions, while thermal desorption studies indicate that the steps and ledges become preferentially covered in others.

As a result of our catalyzed hydrocarbon conversion reaction studies on platinum crystal surfaces, a model has been developed for the working platinum reforming catalyst and is shown in Figure 15. Between 80% and 90% of the catalyst surfaces covered with an irreversibly adsorbed carbonaceous

deposit that stays on the surface for times much longer than the reaction turnover time.[31] The structure of this carbonaceous deposit varies continuously from two dimensional to three dimensional with increasing reaction temperature, and there are platinum patches that are not covered by this deposit. These metal sites can accept the reactive molecules and are responsible for the observed structure sensitivity and turnover rates. While there is evidence that the carbonaceous deposit participate in some of the reactions by hydrogen transfer by providing sites for rearrangement and desorption while remaining inactive in other reactions, its chemical role requires further exploration.

The oxidation state of surface atoms is also very important to control both the activity and selectivity of catalytic reactions. For example, rhodium was reported to yield predominantly acetaldehyde and acetic acid, when prepared under appropriate experimental conditions during the reaction of carbon monoxide and hydrogen.[33] Our studies using unsupported polycrystalline rhodium foils detected mostly methane,[34] along with small amounts of ethylene and propylene under very similar experimental conditions. It appears that most of the organic molecules form following the dissociation of carbon monoxide by the rehydrogenation of CH_x units in the manner similar to alkane and alkene production from CO/H_2 mixtures over other more active transition metal catalysts, iron, ruthenium and nickel. However, when rhodium oxide Rh_2O_3 was utilized as a catalyst, large concentrations of oxygenated C_2 or C_3 hydrocarbons were produced, including ethanol, acetaldehyde and propionaldehyde. Furthermore, the addition

of C_2H_4 to the CO/H_2 mixture yielded propionaldehyde indicating the carbonylation ability of Rh_2O_3. Under similar experimental conditions over the rhodium metal, C_2H_4 was quantitatively hydrogenated to ethane and the carbonylation activity was totally absent. Clearly, higher oxidation state rhodium ions are necessary to produce the oxygenated organic molecules. Unfortunately Rh_2O_3 reduced rapidly in the CO/H_2 mixture to a metallic state with drastic alteration of the product distribution from oxygenated hydrocarbons to methane. In order to stabilize the rhodium ion lanthanum rodate ($LaRhO_3$) was prepared by incorporating Rh_2O_3 into La_2O_3 at high temperatures.[36] Over this stable catalyst the formation of oxygenated products from CO and H_2 predominated. The reason for the change of selectivity in CO/H_2 reactions with alteration of the oxidation state of the transition metal is due largely to the change of heats of adsorption of CO and H_2 as the oxidation state of the transition metal ion is varied. This is demonstrated in Figure 16. The CO adsorption energy is decreased upon oxidation and the heat of adsorption of D_2 is increased presumably due to the formation of a hydroxide. In addition, the metal is primarily active for hydrogenation and CO dissociation while the oxide can perform carbonylation and has reduced hydrogenation activity. There are many examples of changing selectivity and activity of catalyst as the oxidation state of the transition metal ion is varied. This is clearly one of the important ingredients for heterogeneous catalysis.

As a result of these findings and others during the period of 1976 to the present, we could identify three molecular ingredients that control catalytic properties. These are the <u>atomic surface structure</u>, an <u>active</u>

carbonaceous deposit and the proper oxidation state of surface atoms. As a result of these studies we have also developed a model for the working platinum catalyst.

Much of the research in physical sciences and certainly everthing I described as our work during the period of 1965-78 is using the passive approach. The purpose is to understand, in my case, to understand the molecular ingredients of heterogeneous catalysis. In all these investigations very little if any thought is given as to how to use the understanding that was obtained. During the last three years I am attempting to carry out more and more active research in two ways:
(1) To use the knowledge gained to build a better catalyst system. Additives are being used to alter beneficially the surface structure to reduce the amount of carbon deposit or to slow down its conversion to the inactive graphitic form. Bimetallic or multimetallic catalyst systems have been prepared and studied in my laboratory and elsewhere. By the addition of one or more other transition metals (paladium, iridium, rhenium or gold) to platinum, the alloy catalyzed system can be operated at higher reaction temperatures to obtain higher reaction rates. They show slower rates of deactivation (have longer lifetimes) and can also be more selective for a given chemical reaction (dehydrocyclization or isomerization) than the one component catalyst. For example, the addition of small amounts of gold to platinum increased the isomerization activity[37] while drastically reduced the dehydrocyclization activity of this catalyst (Figure 17). The addition of potassium changes the binding energy of carbon monoxide drastically by changing the charge density of the transition metal surface atoms which molecular orbitals of carbon monoxide.[38] We

have explored in great detail the effect of alkali atoms on transition metal surfaces both in accelerating or inhibiting various chemical reactions. In Figure 18 and 19 we show examples of how alkali metal addition changes the bonding of carbon monoxide on platinum surfaces[39] while increasing the activation energy for C-H bond breaking on platinum surfaces.[40] In the former case the carbon monoxide dissociation reaction is definitely facilitated by the presence of potassium. In the latter case potassium is a uniform poison for hydrocarbon conversion reactions on platinum surfaces. We are also attempting to formulate and build new catalysts by incorporating transition metal ions into refractory oxide lattices. This way we stabilize the transition metal high oxidation state under reducing reaction conditions.

As combined surface science and catalytic reaction studies develop and working models for catalysts help to build new catalysts, the field is becoming high technology catalysis science. This transition from art to catalysis science could not have come soon enough. Rapidly rising cost of petroleum necessitates the use of new fuel sources such as coal, shale and tar sand and the use of new feedstocks for chemicals including CO and H_2 and coal liquids. The new fuel and chemical technologies based on these new feedstocks require the development of an entirely new generation of catalysts. Ultimately, our fuel and chemicals must be produced from the most stable and abundant molecules on our planet, among them

carbon dioxide, water, nitrogen and oxygen. To build the catalytic chemistry starting from these species is a considerable challenge that I believe will be met by the catalysis science in the future. (2) This brings me to another a new approach of active research in catalysis science which is really a very old one indeed. We are attempting to find catalysts for chemical reactions of small molecules that have not been explored. In Figure 20 and 21 we show several chemical reactions of small molecules, most of them are thermodynamically feasible. Yet, their catalytic science have not been explored. The two reactions that require the input of extra energy, the splitting of water to hydrogen and oxygen by solar radiation or the photochemical splitting of carbon dioxide to carbon monoxide and oxygen are important reactions and major challenges that could be met by clever catalytic chemists and surface scientists. The reduction of carbon dioxide to formic acid, the reactions of nitrogen with oxygen and water to form nitric acid and the partial oxidation of methane to formaldehyde and methanol and the reaction of water with graphite to produce methane are among those very important reactions to produce fuels and chemicals that are yet to be explored from the point of view of catalytic scientists. While in the beginning of the century, much of the science was developed by searching for catalysts to carry out important reactions that were thermodynamically feasible, this approach was abandoned in the last thirty to forty years. I believe that with our increased more detailed knowledge of catalysts and catalysis science, perhaps we can embark again on searching for catalysts for important reactions that have not been utilized in the chemical technology as yet. The future is indeed unlimited and bright for molecular surface science and its application to catalysis science.

There are many other applied areas of surface science where molecular surface science has hardly been employed: lubrication, chemical corrosion, radiation damage and adhesion are among them. It is my hope that by combining techniques and knowledge in molecular surface science and in one of these applied fields, major advances will be made that will bring these fields to high technology where science leads the development of the technology. The solid-liquid interface is an area that requires intense exploration in the near future. Clearly, developments in electrochemistry and biology depend on our ability to scrutinize on the molecular level the solid-liquid interface. Surface science studies of solid-solid interfaces could produce major advances in the fields of coatings and composites. The opportunities are virtually unlimited for clever surface scientists who are willing to be broad enough to learn about applications of their molecular level studies to important fields and technologies that are based on surface science.

ACKNOWLEDGEMENTS:

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TABLE I : Surface Composition Of Alloys: Experimental Results And Predictions Of The Regular Solution Models

		Segregating Constituent	
		Predicted	
Alloy Systems	Phase Diagram	Regular Solution	Experimental
Ag-Pd	simple	Ag	Ag
Ag-Au	simple	Ag	Ag
Au-Pd	simple	Au	Au
Ni-Pd	simple	Pd	Pd
Fe-Cr	low-T phase	Cr	Cr
Au-Cu	low-T ordered phases	Cu	Au, none, or Cu, depending on composition
Cu-Ni	low-T miscibility gap	Cu	Cu
Au-Ni	miscibility gap	Au	Au
Au-Pt	miscibility gap	Au	Au
Pb-In	intermediate phase	Pb	Pb
Au-In	complex	In	In
Al-Cu	complex	Al	Al
Pt-Sn	complex	Sn	Sn
Fe-Sn	complex	Sn	Sn
Au-Sn	complex	Sn	Sn

FIGURE CAPTIONS

1. A. Diffraction pattern from the reconstructed platinum (100) surface.

   B. Schematic representation of the (100) surface with the (5 x 1) surface structure.

   C. Diffraction pattern from the unreconstructed platinum (100) surface.

   D. Schematic representation of the unreconstructed (100) surface.

2. Structure of the reconstructed platinum (100) crystal face as solved by surface crystallography.

3. The ideal and regular solid solution models for a binary system that predict surface segregation of the constituent with lower surface free energy.

4. Surface excess of silver as a function of bulk composition and layer by layer in silver-gold alloys.

Table 1: Surface composition of alloys, experimental results and prediction of the regular solution models.

5. Scheme of the molecular beam surface scattering experiment.

6. Structure of several high Miller Index stepped surfaces with different terrace widths and step orientations.

7. Surface structures of several high Miller Index surfaces with deferring kink concentrations in the steps.

8. HD production during H_2/D_2 mixed molecular beam scattering, as a function of angle of incidence. Intensity of the HD molecular beam is normalized to the incident D_2 intensity. A) The Pt(332) surface with the stepped edges perpendicular to the incident beam ($\phi = 90°$), shows the highest reactivity. B) The Pt(332) surface where the projection of the beam on the surface is parallel to the step edges, $\phi = 0°$, is also shown. C) The Pt(111) surface exhibits almost an order of magnitude lower activity.

9. Schematic representation of the experimental apparatus to carry out the catalytic reaction rate studies on single crystal or polycrystalline surfaces of low surface area at low and high pressures in the 10^{-7} to 10^{+4} torr range.

10. Skeletal rearrangement reactions of hydrocarbons are catalyzed by platinum with high activity and unique selectivity. Depicted here are the several reaction pathways which occur simultaneously during the catalyzed conversion of n-hexane (C_6H_{14}). The isomerization, cyclization and aromatization reactions that produce branched or cyclic products are important in the production of high octane gasoline from petroleum naphta. The hydrogen analysis reaction involves C-C bond breaking yields undesirable gaseous products.

11. Dehydrocyclization of alkanes to aromatic hydrocarbons is one of the most important petroleum reforming reactions. The bar graph shown here compare reaction rates for n-hexane and n-heptane aromatization catalyzed at 573K and atmospheric pressure over the two flat platinum single crystal faces with different atomic structure. The platinum surface with hexagonal atomic arrangement is several times more active than the surface with a square unit cell over a wide range of reaction conditions.

12. Reaction rates are shown as a function of surface structure for isobutane isomerization and hydrogenolysis catalyzed at 570K and atmospheric pressure over the four platinum surfaces. The rate for both reaction pathways are very sensitive to structural features of the model single crystal surfaces. Isomerization is favored on the

platinum surfaces that have a square (100) atomic arrangement. Hydrogenolysis rates are maximized when kink sites are present in high concentration as in the platinum (10,8,7) crystal surface.

13. Surface structure sensitivity of iron catalyzed ammonia synthesis.

14. Carbon-14 labelled ethylene C_2H_4 was chemisorbed as a function of temperature on a flat platinum surface with hexagonal orientation. The hydrogen/carbon composition of the adsorbed species was determined from hydrogen thermal desorption studies. The amount of preadsorbed ethylene that could not be removed by subsequent treatment in one atmosphere of hydrogen represents the "irreversibly adsorbed fraction." The adsorption reversibility decreases markedly with increasing adsorption temperature as the surface species become more hydrogen deficient. The irreversibly adsorbed species have very long surface residence times of the order of days.

15. Model for the working platinum catalyst that was developed from our combination of surface studies using single crystal surfaces and hydrocarbon reaction rate studies on these same surfaces.

16. Heat of desorption of CO and D_2 from La_2O_3 fresh and used, $LaRhO_3$ fresh and used, Rh_2O_3 fresh and used and Rh metal. The spread of each value represents the variation with surface coverage rather than experimental uncertainty.

17. The rate of formation of various products from n-hexane as a function of fractional gold surface coverage or gold platinum alloys that were prepared by vaporizing and diffusing gold into platinum (111) crystal surfaces.

18. Vibrational spectra of the saturation CO coverage adsorbed on platinum (111) at 300K as a function of preadsorbed potassium coverage.
19. Activation energy of the hydrogen β - elimination from carbonaceous deposits after n-hexane reactions over Pt (111) surfaces as a function of potassium coverages.
20. Standard free energies for several chemical reactions.
21. Standard free energies for several chemical reactions.

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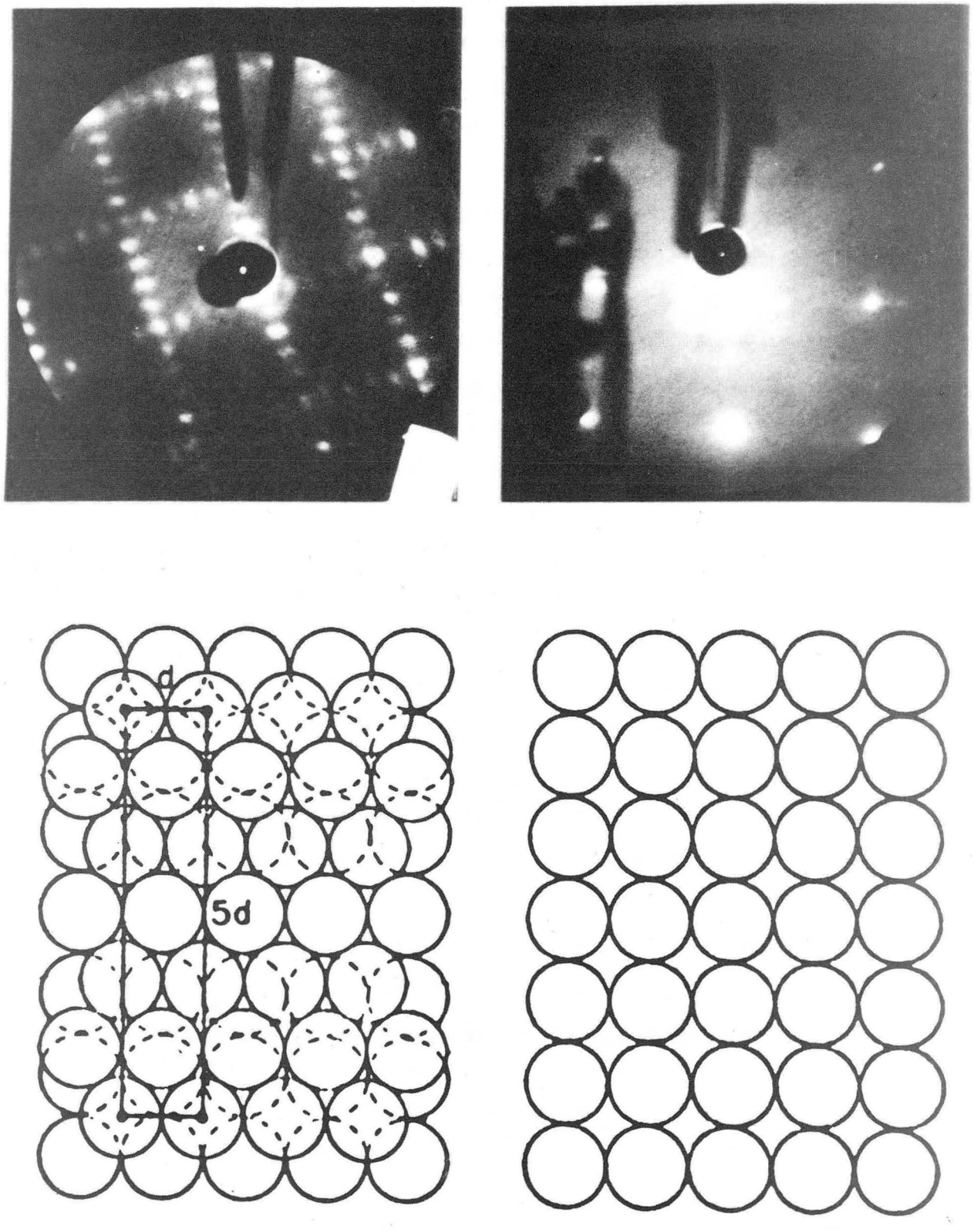
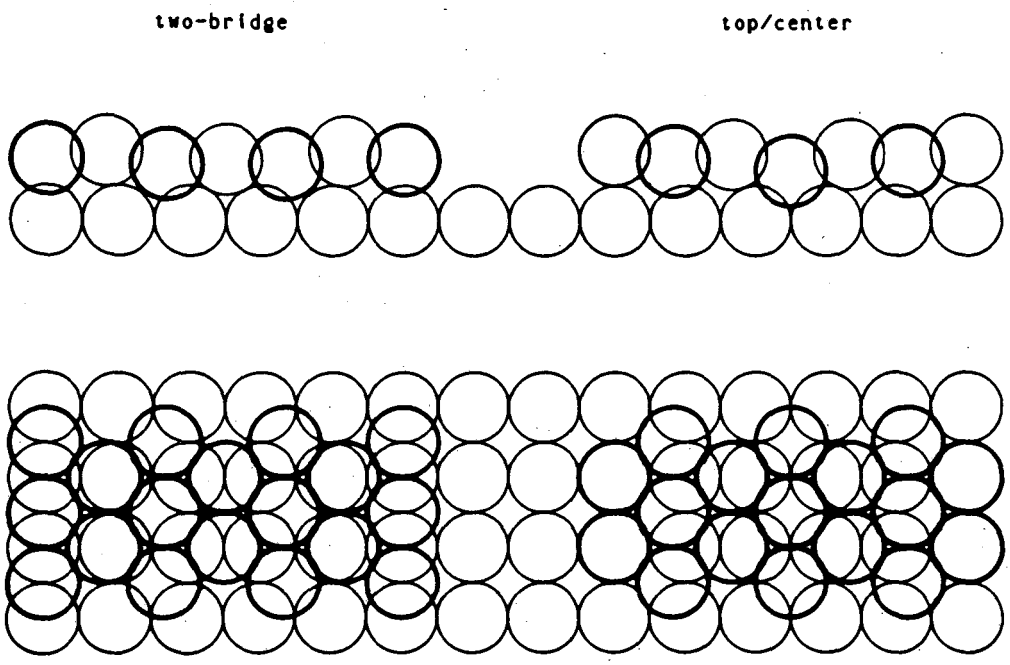


XBB 710-5356

Fig. 1

fcc (100) : buckled hexagonal top layer



XBL 7912-13739

Fig. 2

For an ideal solid solution:

$$\frac{x_2^s}{x_1^s} = \frac{x_2^b}{x_1^b} \exp\left[\frac{(\sigma_1 - \sigma_2)a}{RT}\right]$$

For a regular solid solution:

$$\frac{x_2^s}{x_1^s} = \frac{x_2^b}{x_1^b} \exp\left[\frac{(\sigma_1 - \sigma_2)a}{RT}\right] \exp\left\{\frac{\Omega(\ell + m)}{RT}\left[(x_1^b)^2 - (x_2^b)^2\right] - \frac{\Omega\ell}{RT}\left[(x_2^s)^2 - (x_1^s)^2\right]\right\}$$

where Ω = regular solution parameter = $\dfrac{\Delta H_{mixing}}{x_1^b \cdot x_2^b}$

ℓ = fraction of nearest neighbors in surface layer.

m = fraction of nearest neighbors in adjacent layer.

XBL 741-234

Fig. 3

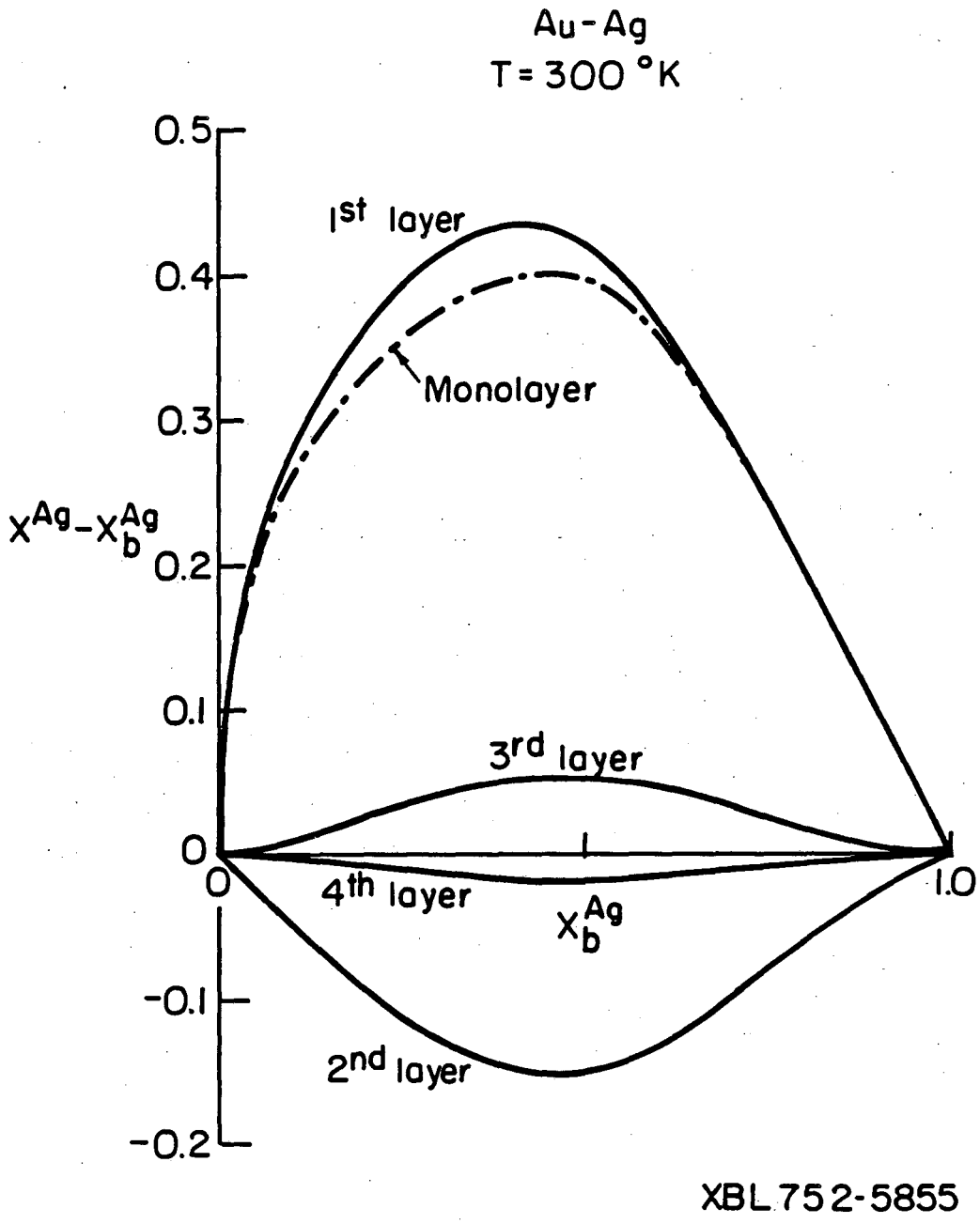
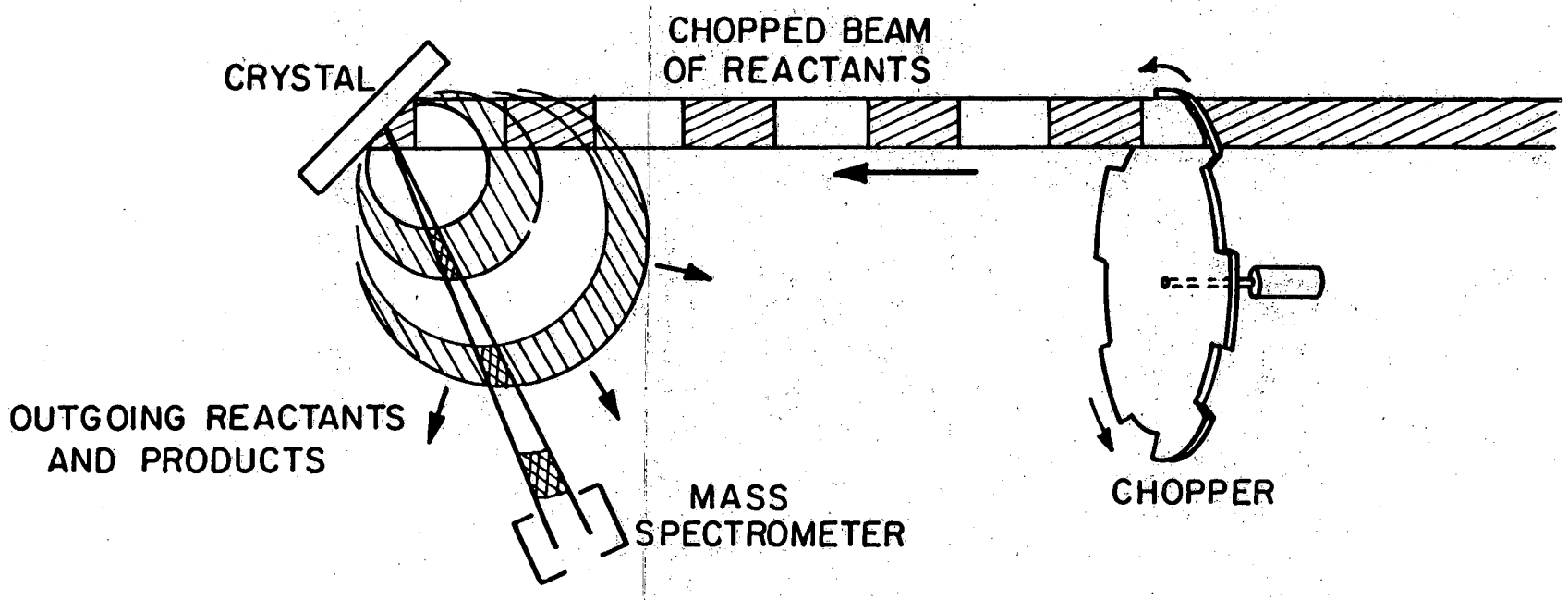

Au-Ag
T = 300 °K
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
$X^{Ag} - X_b^{Ag}$
1st layer
Monolayer
3rd layer
4th layer
2nd layer
0
1.0
X_b^{Ag}
XBL 752-5855

Fig. 4



XBL 772-5082

Fig. 5

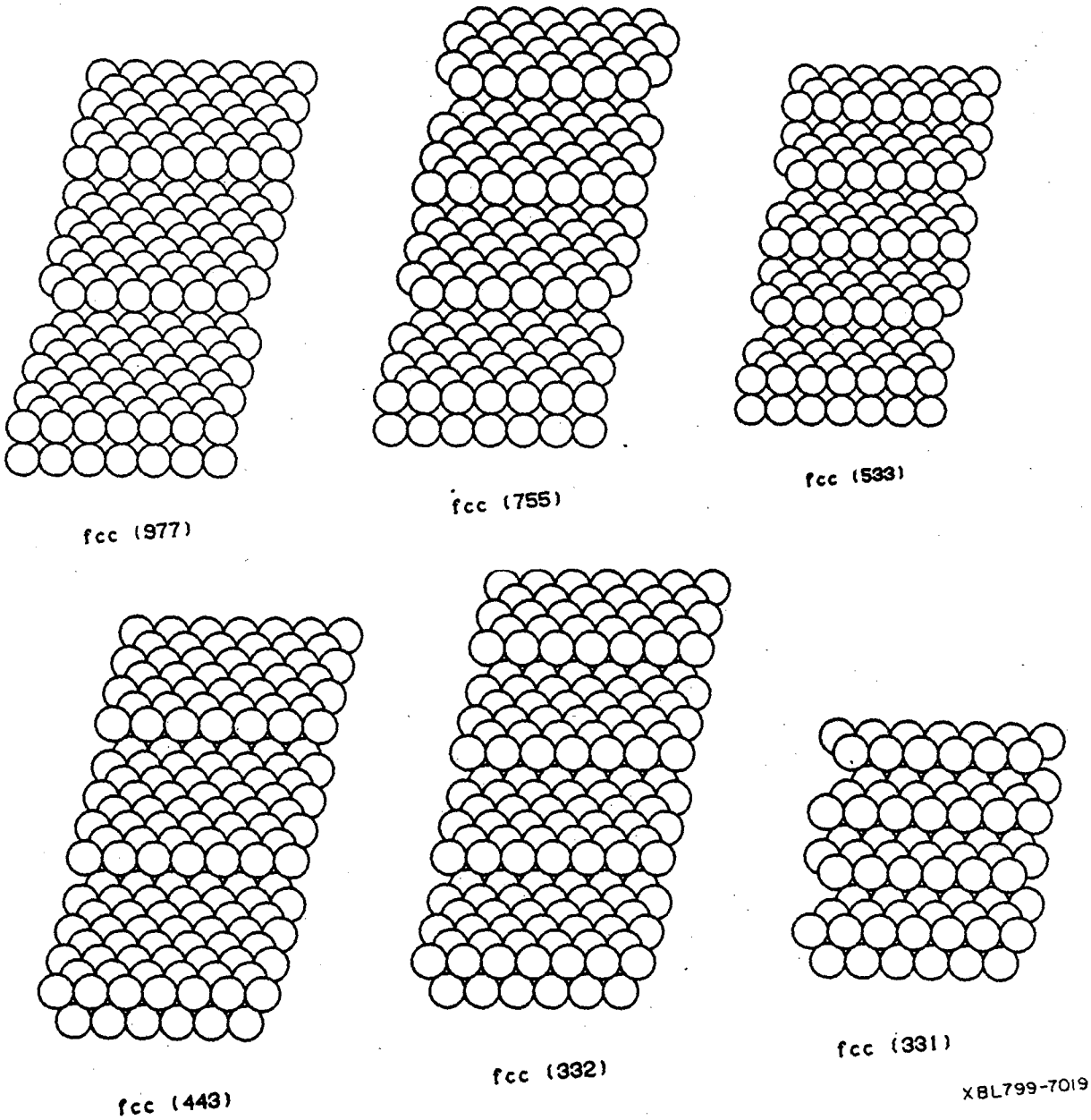


Fig. 6

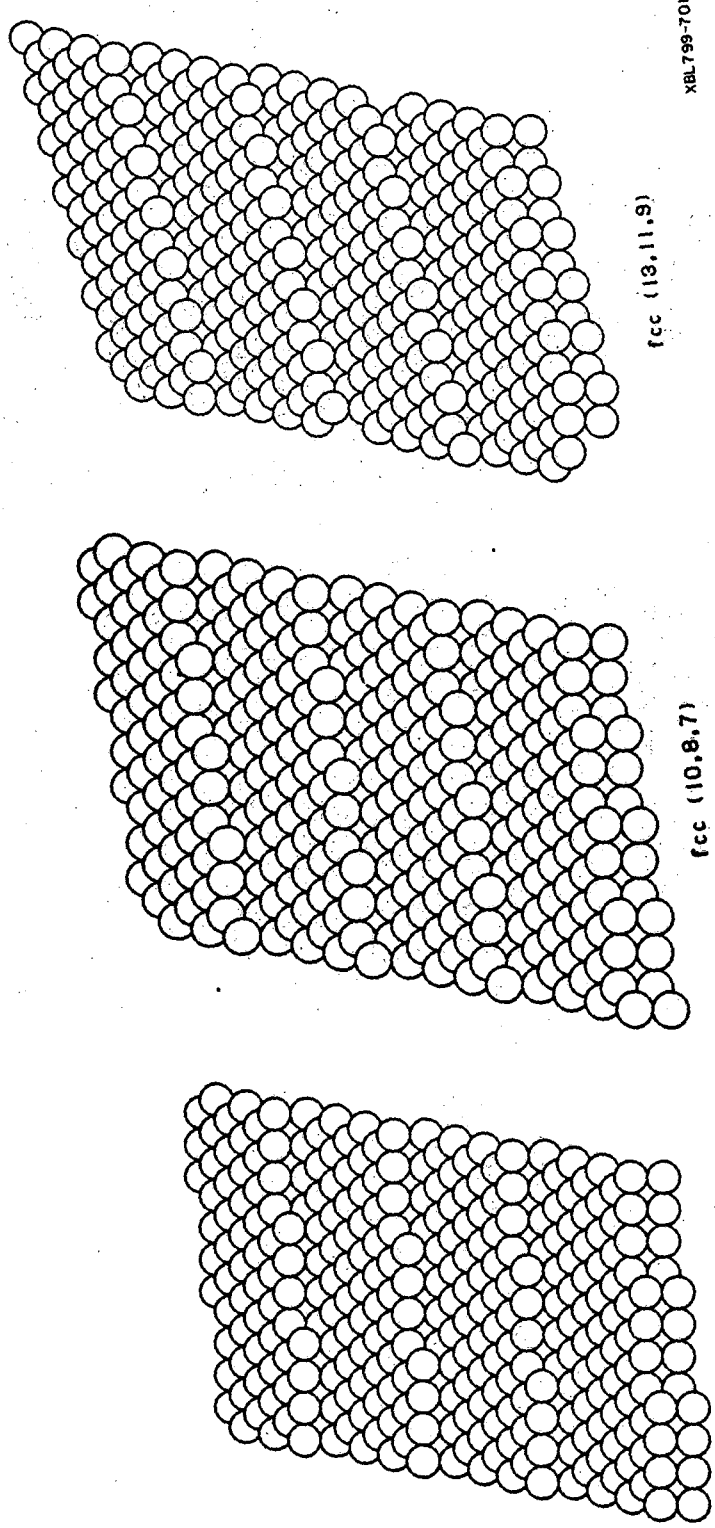
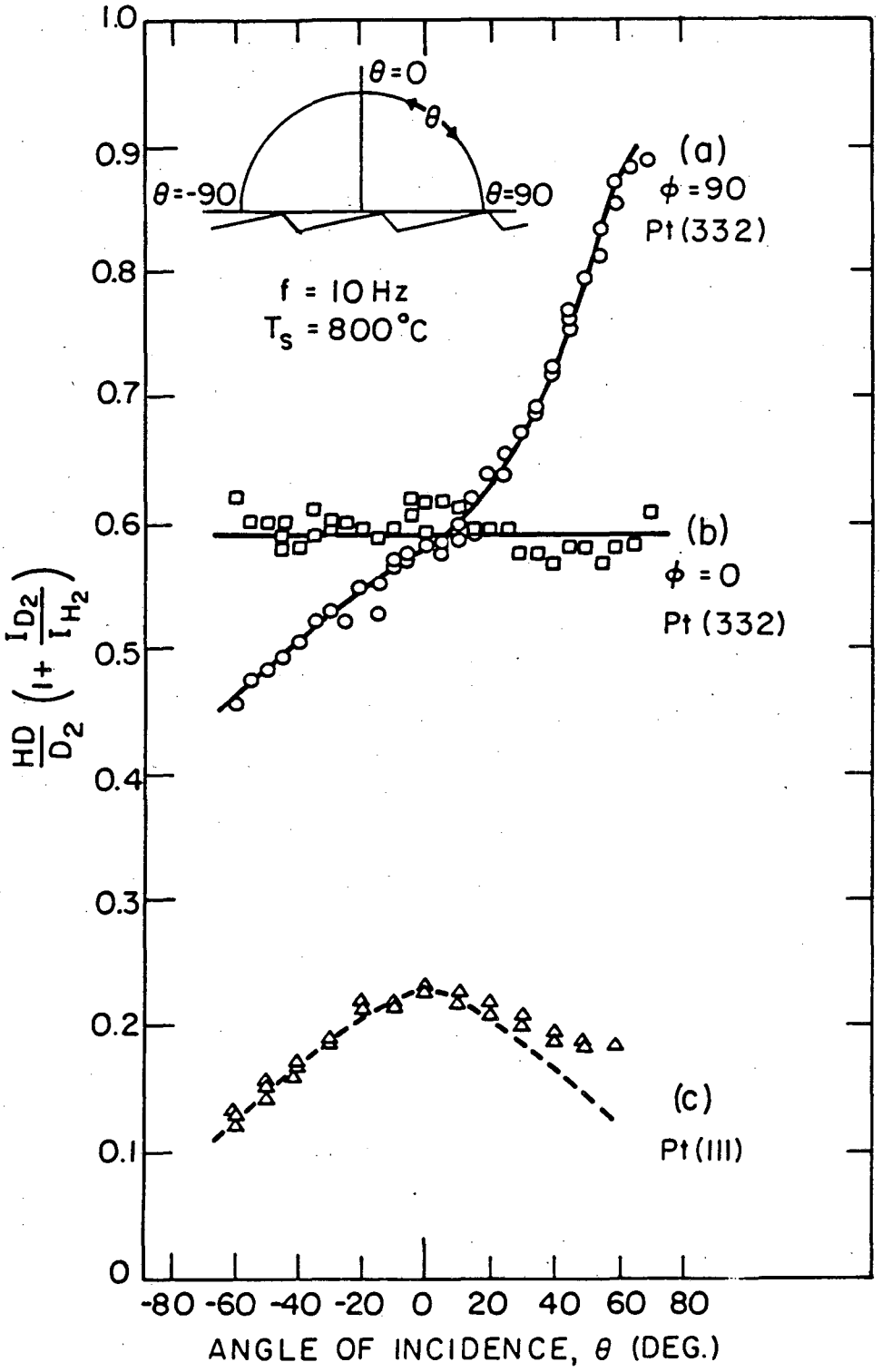


Fig. 7



XBL772-5084A

Fig. 8

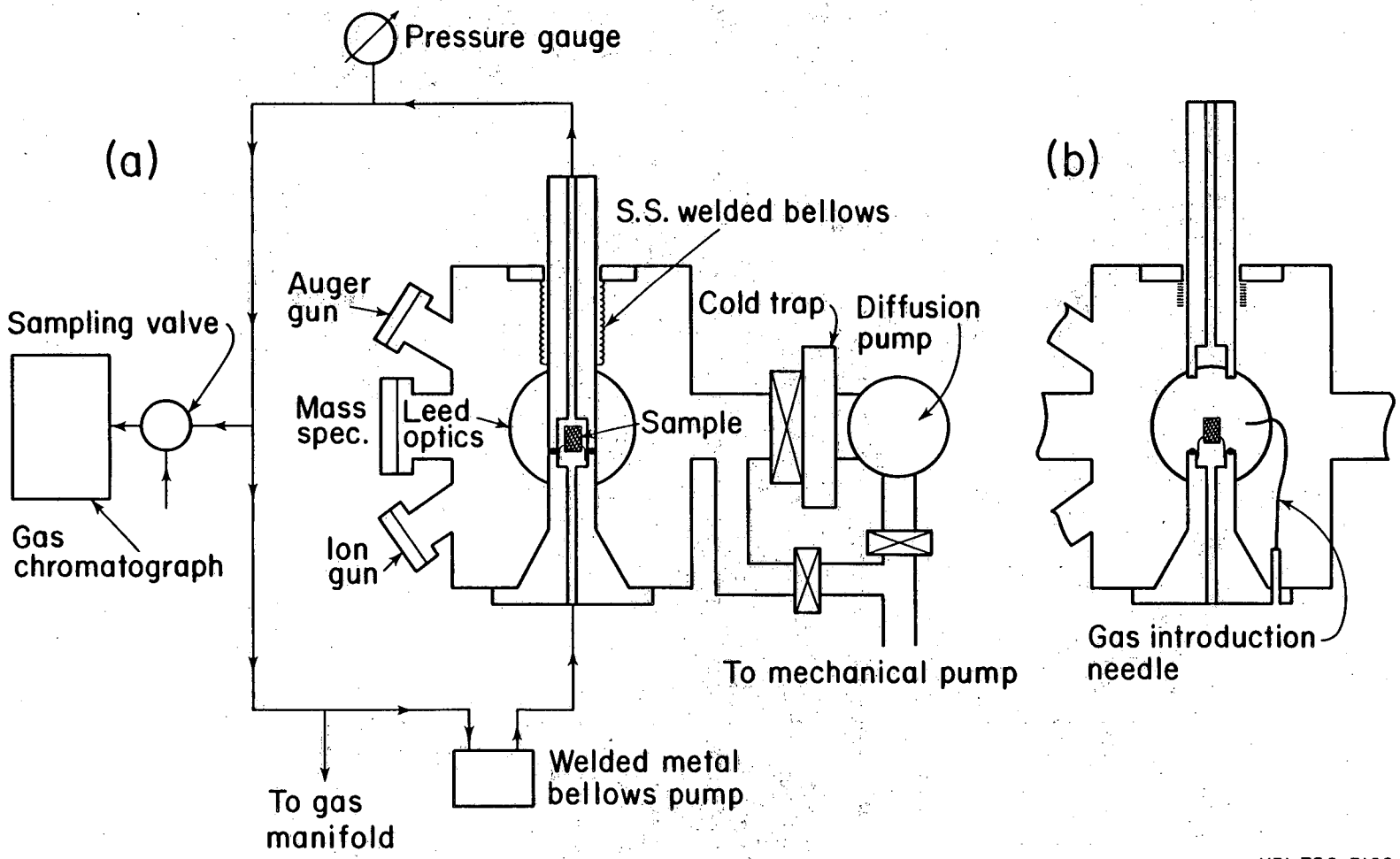

(a)
Pressure gauge
S.S. welded bellows
Auger gun
Sampling valve
Cold trap
Diffusion pump
Mass spec.
Leed optics
Sample
Gas chromatograph
Ion gun
To mechanical pump
To gas manifold
Welded metal bellows pump
(b)
Gas introduction needle
XBL 756-3160

Fig. 9

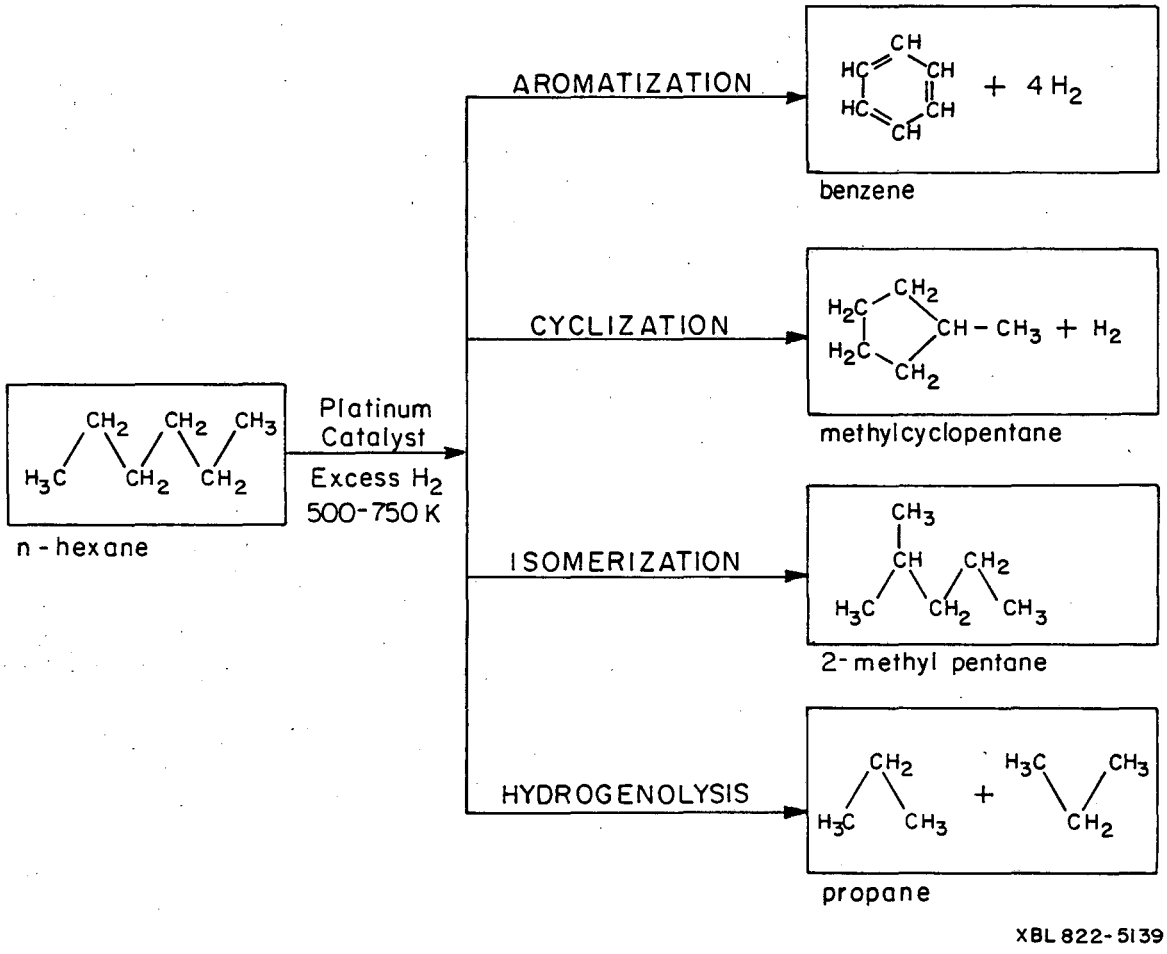

n - hexane
Platinum Catalyst
Excess H_2
500-750 K
AROMATIZATION
benzene
+ 4 H_2
CYCLIZATION
methylcyclopentane
+ H_2
ISOMERIZATION
2-methyl pentane
HYDROGENOLYSIS
propane
XBL 822-5139

Fig. 10

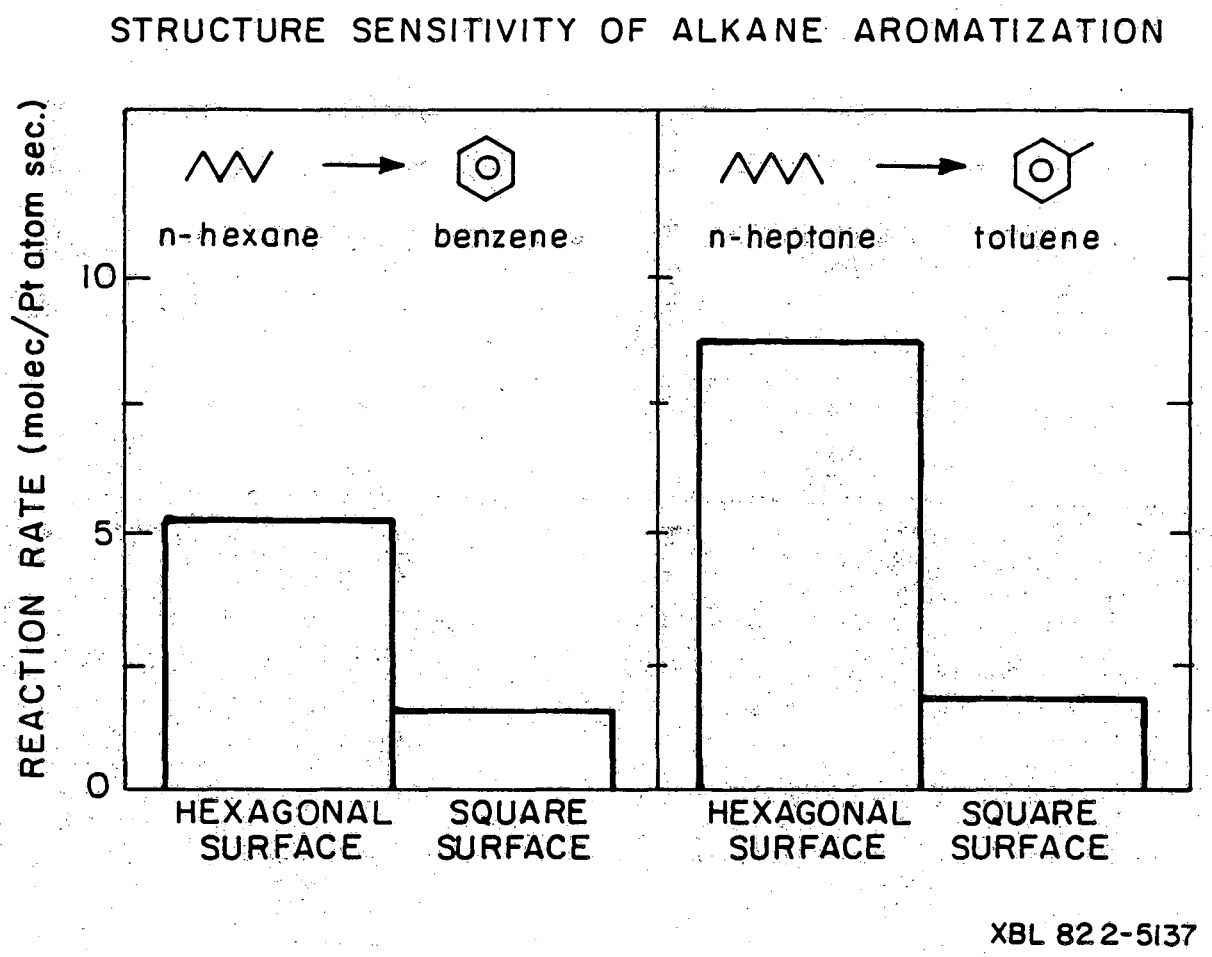
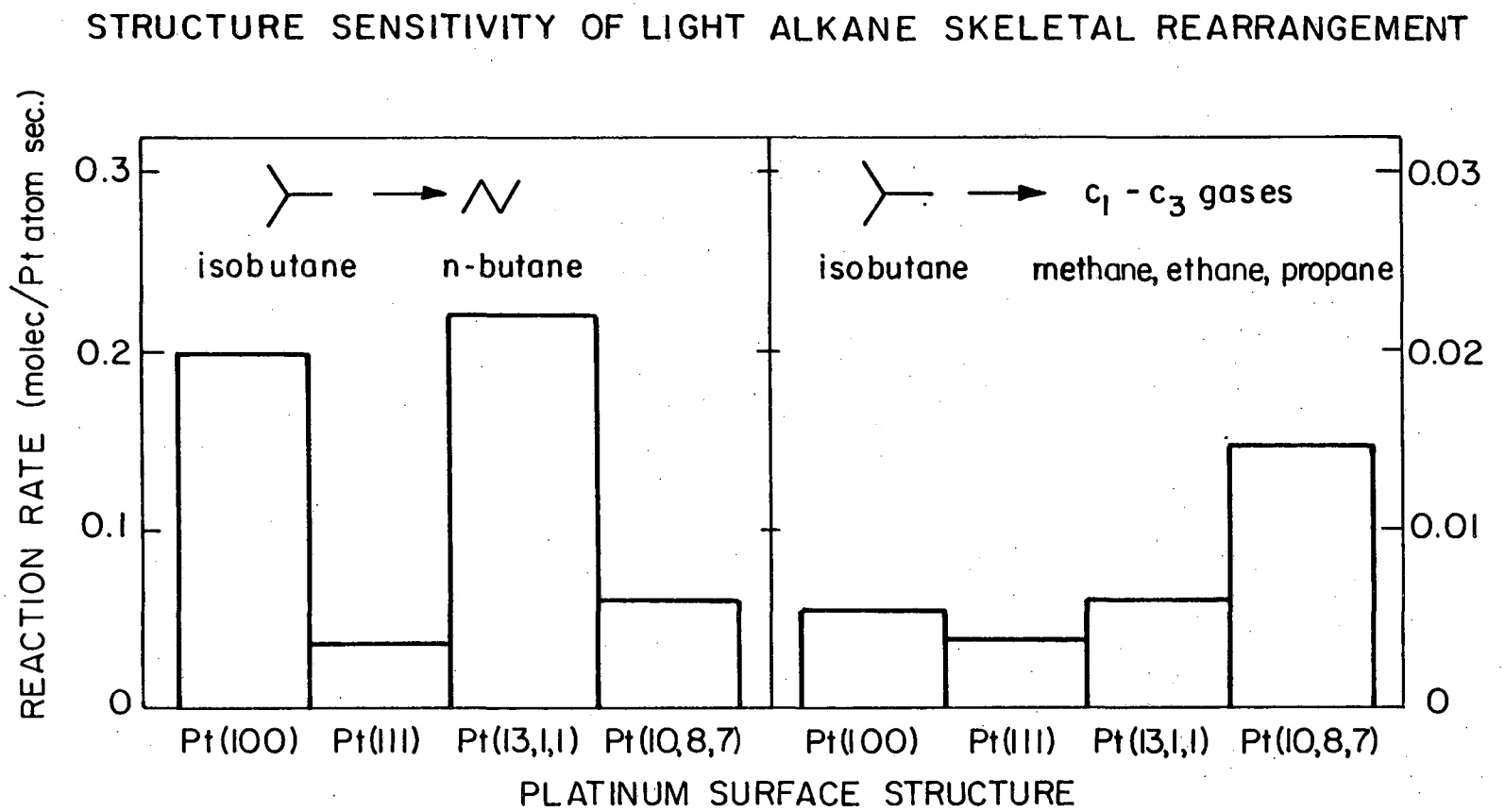

STRUCTURE SENSITIVITY OF ALKANE AROMATIZATION
REACTION RATE (molec/Pt atom sec.)
10
5
0
n-hexane
benzene
n-heptane
toluene
HEXAGONAL SURFACE
SQUARE SURFACE
HEXAGONAL SURFACE
SQUARE SURFACE
XBL 822-5137

Fig. 11



XBL 822-5136

Fig. 12

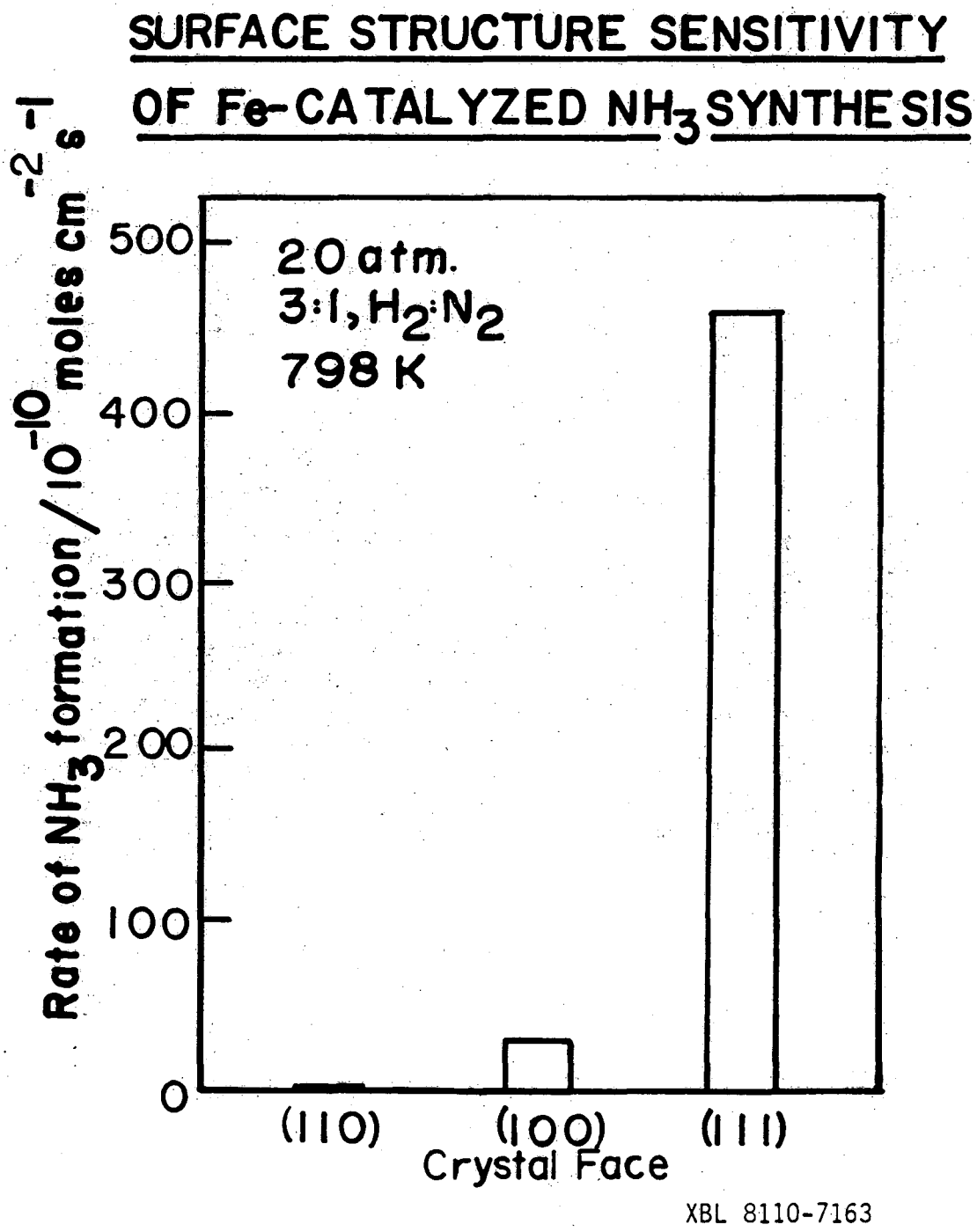

SURFACE STRUCTURE SENSITIVITY
OF Fe-CATALYZED NH3 SYNTHESIS
Rate of NH3 formation / 10^-10 moles cm^-2 s^-1
500
400
300
200
100
0
20 atm.
3:1, H2:N2
798 K
(110)
(100)
(111)
Crystal Face
XBL 8110-7163

Fig. 13

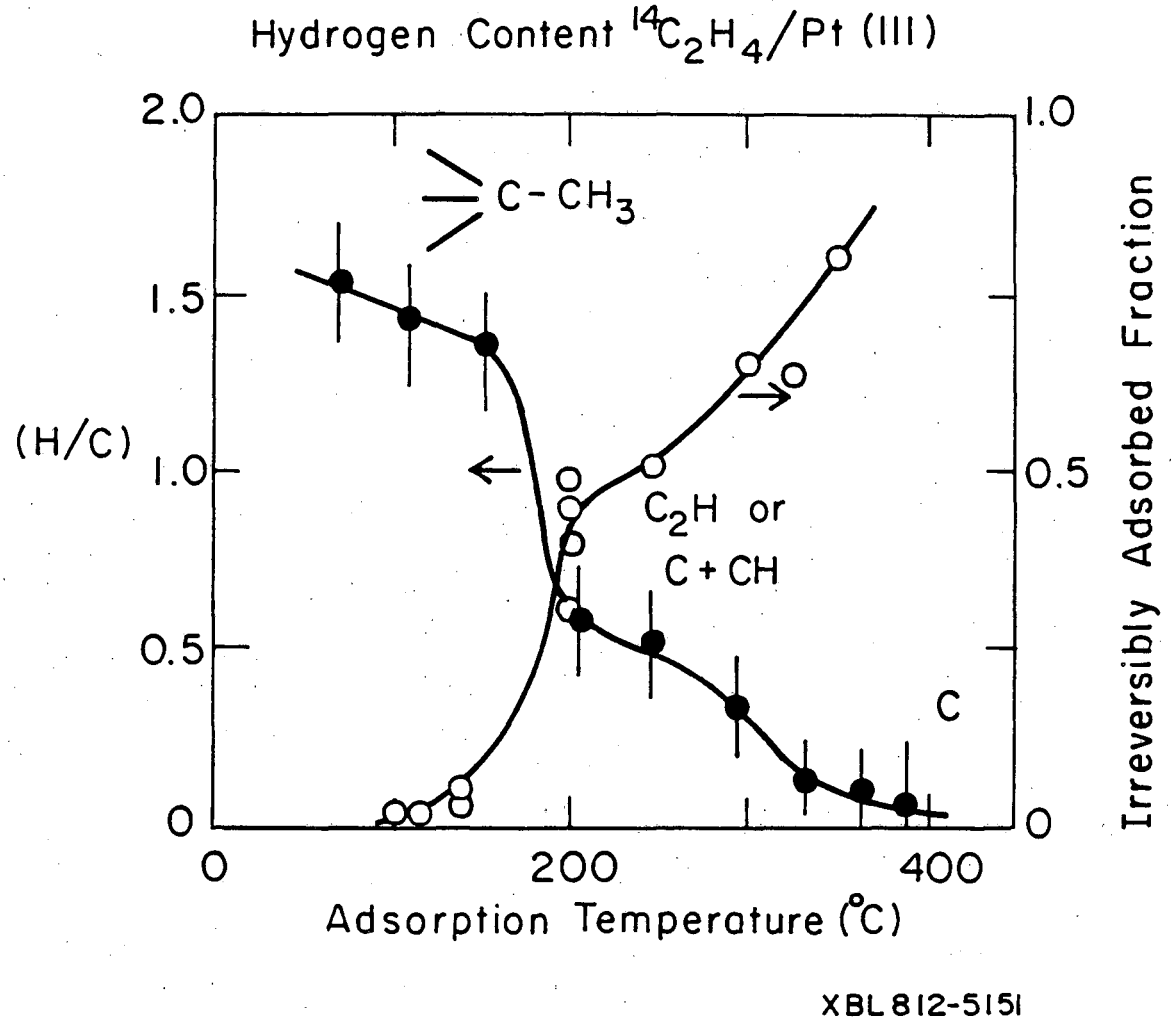

Hydrogen Content $^{14}C_2H_4$/Pt (III)
2.0
1.5
1.0
0.5
0
(H/C)
1.0
0.5
0
Irreversibly Adsorbed Fraction
C-CH3
C2H or
C + CH
C
0
200
400
Adsorption Temperature (°C)
XBL 812-5151

Fig. 14

MODEL FOR THE WORKING PLATINUM CATALYST

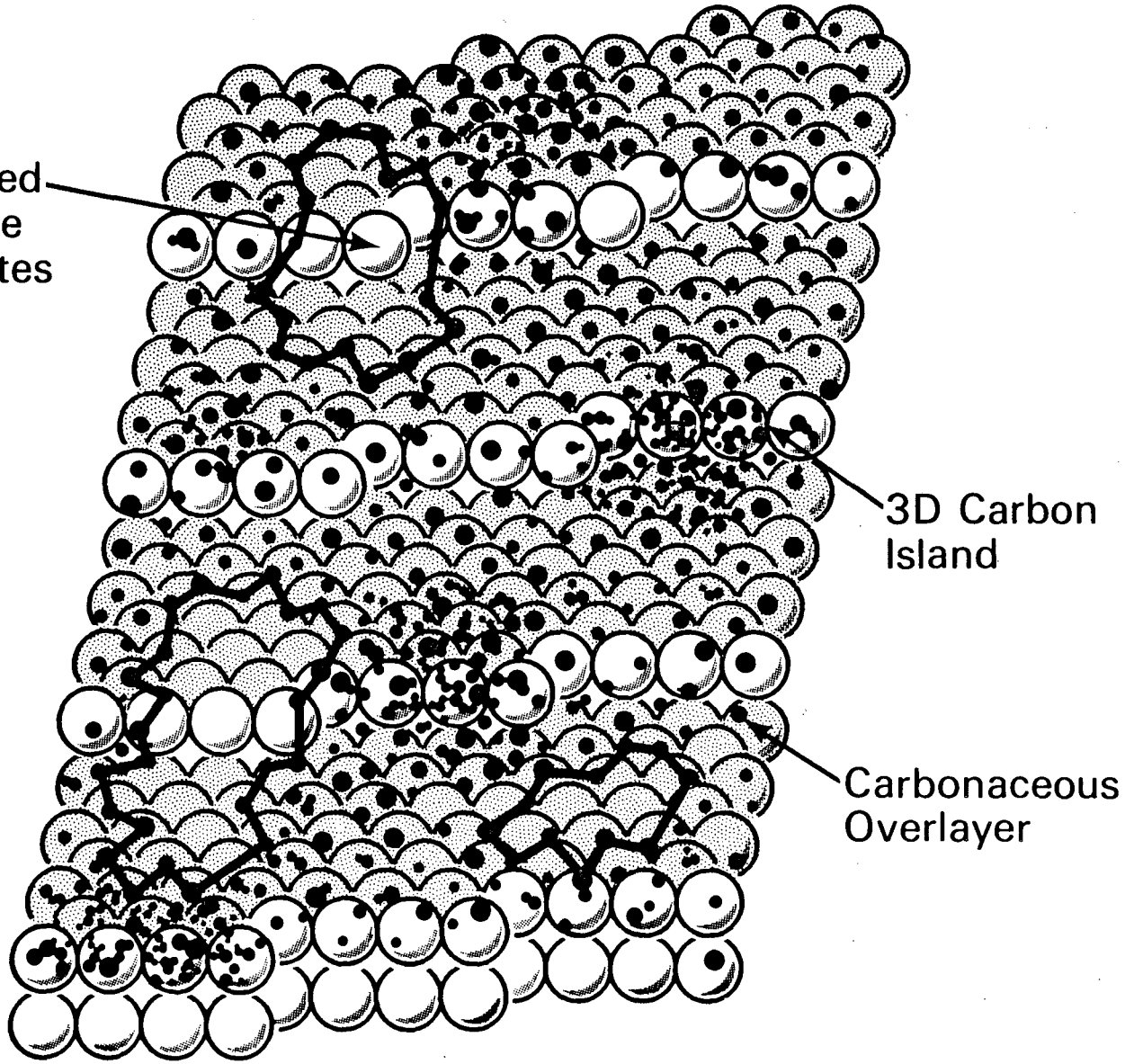
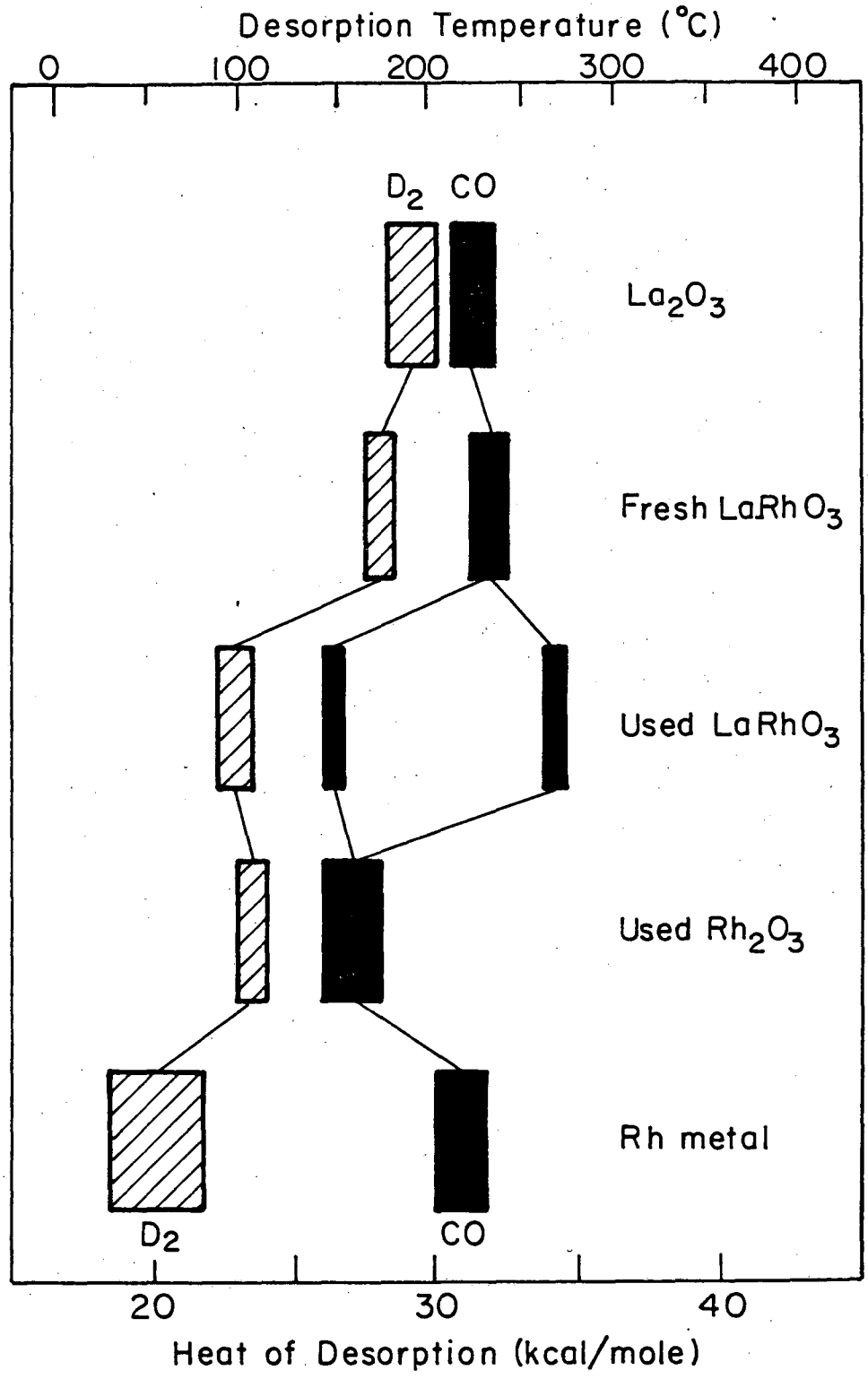
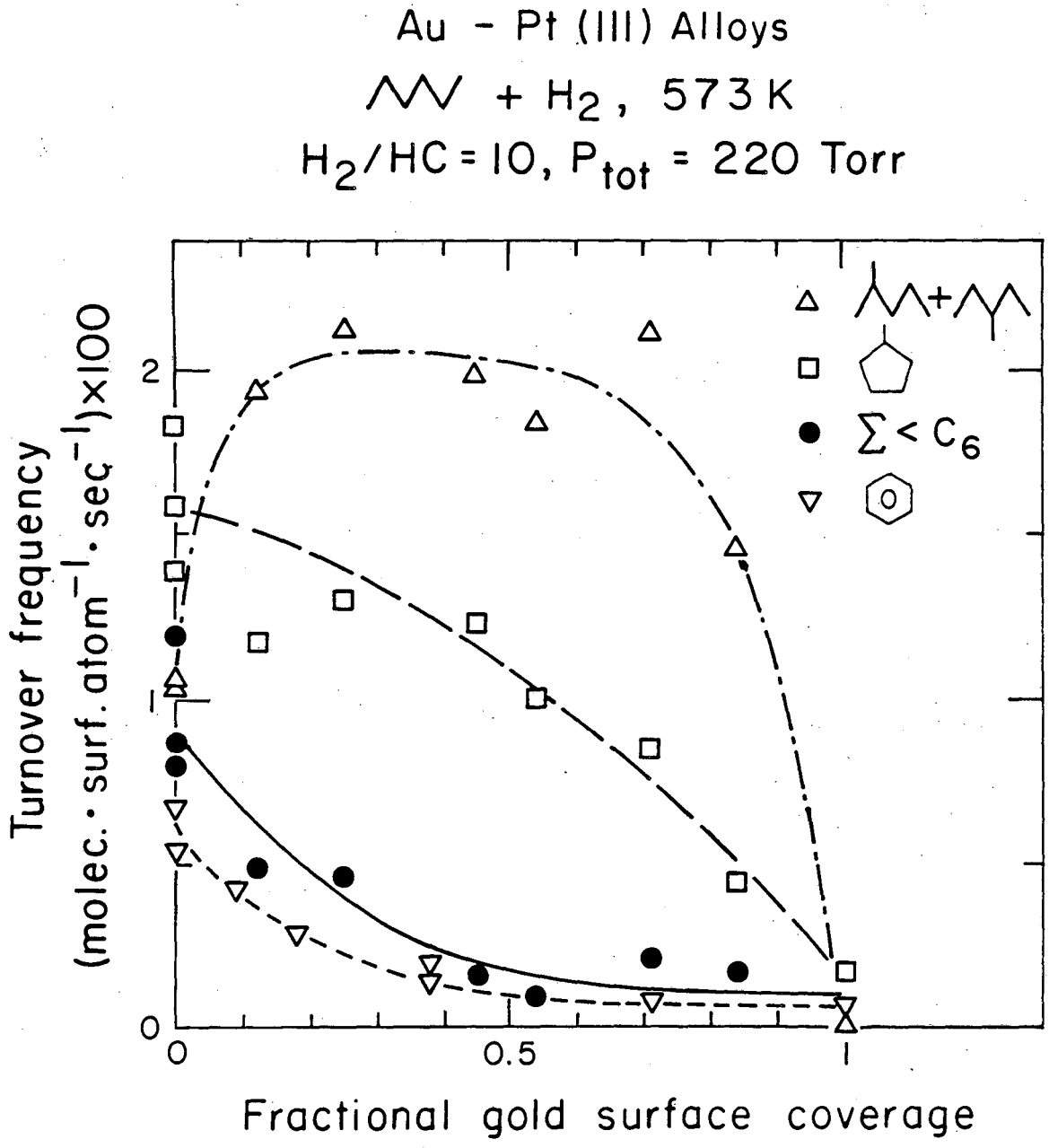


Fig. 15



XBL 817-6123

Fig. 16



XBL 819-2495

Fig. 17

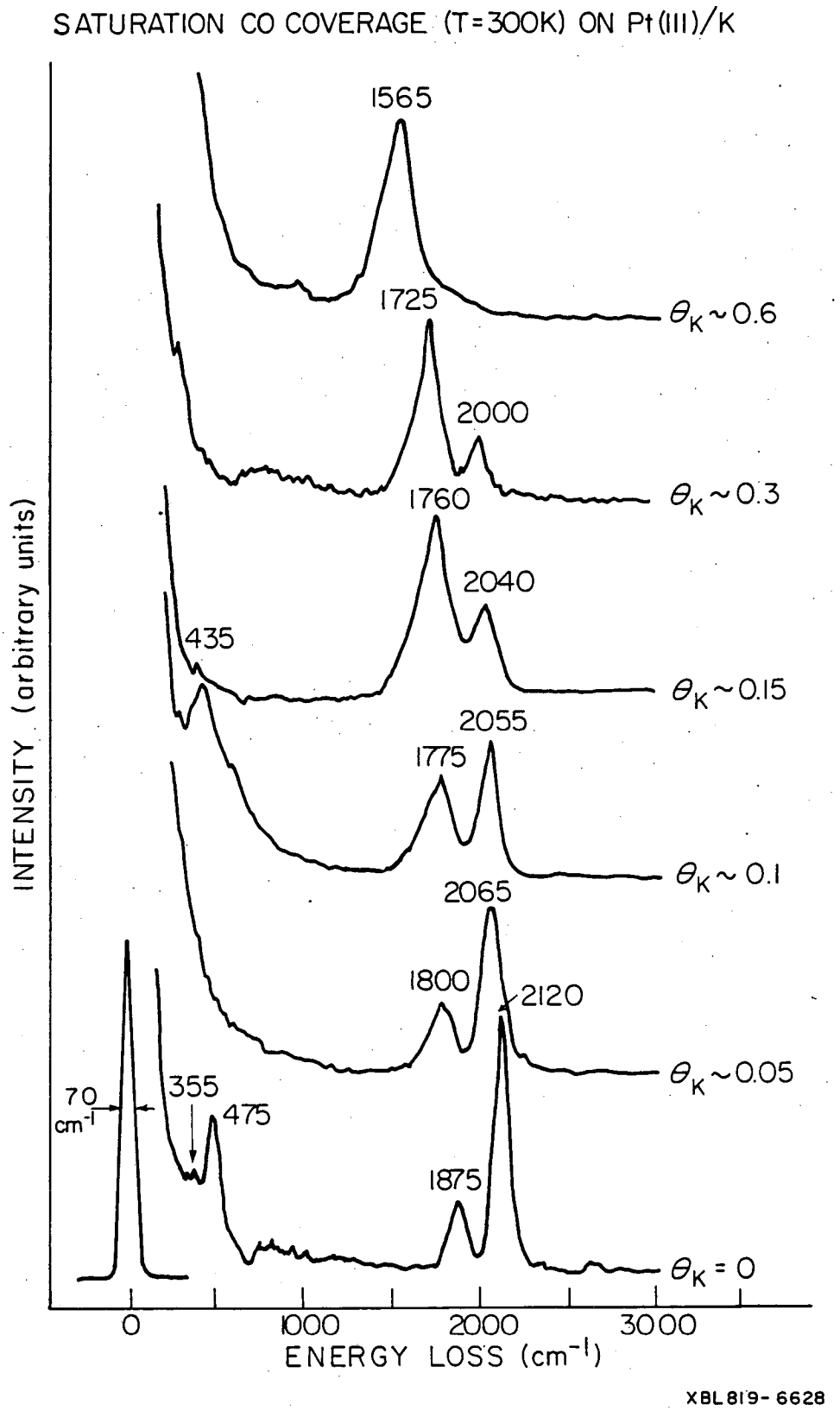
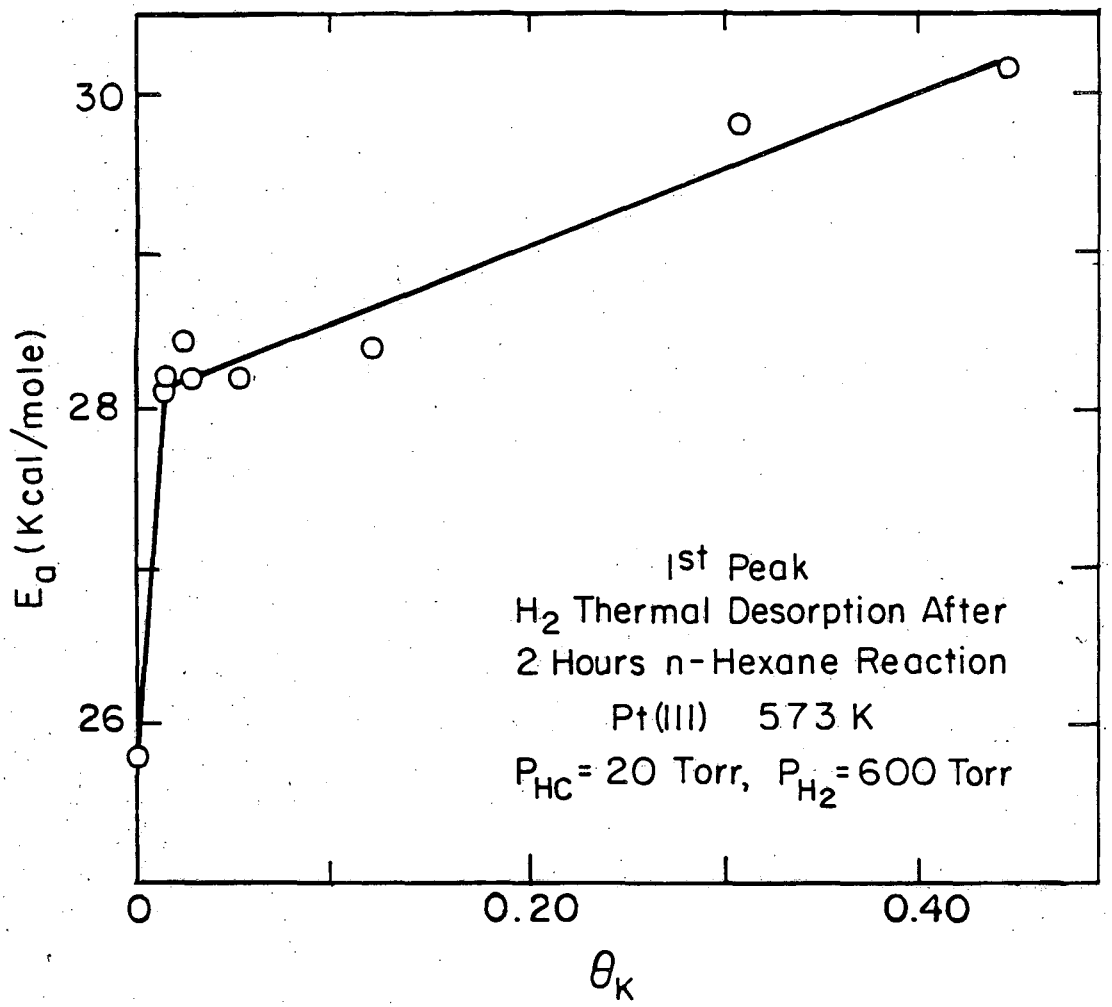

SATURATION CO COVERAGE (T=300K) ON Pt(111)/K
1565
1725
2000
1760
2040
435
2055
1775
2065
1800
2120
355
475
70
cm-1
1875
θK ~ 0.6
θK ~ 0.3
θK ~ 0.15
θK ~ 0.1
θK ~ 0.05
θK = 0
INTENSITY (arbitrary units)
0
1000
2000
3000
ENERGY LOSS (cm-1)
XBL 819-6628

Fig. 18



XBL 823-5304 A

Fig. 19

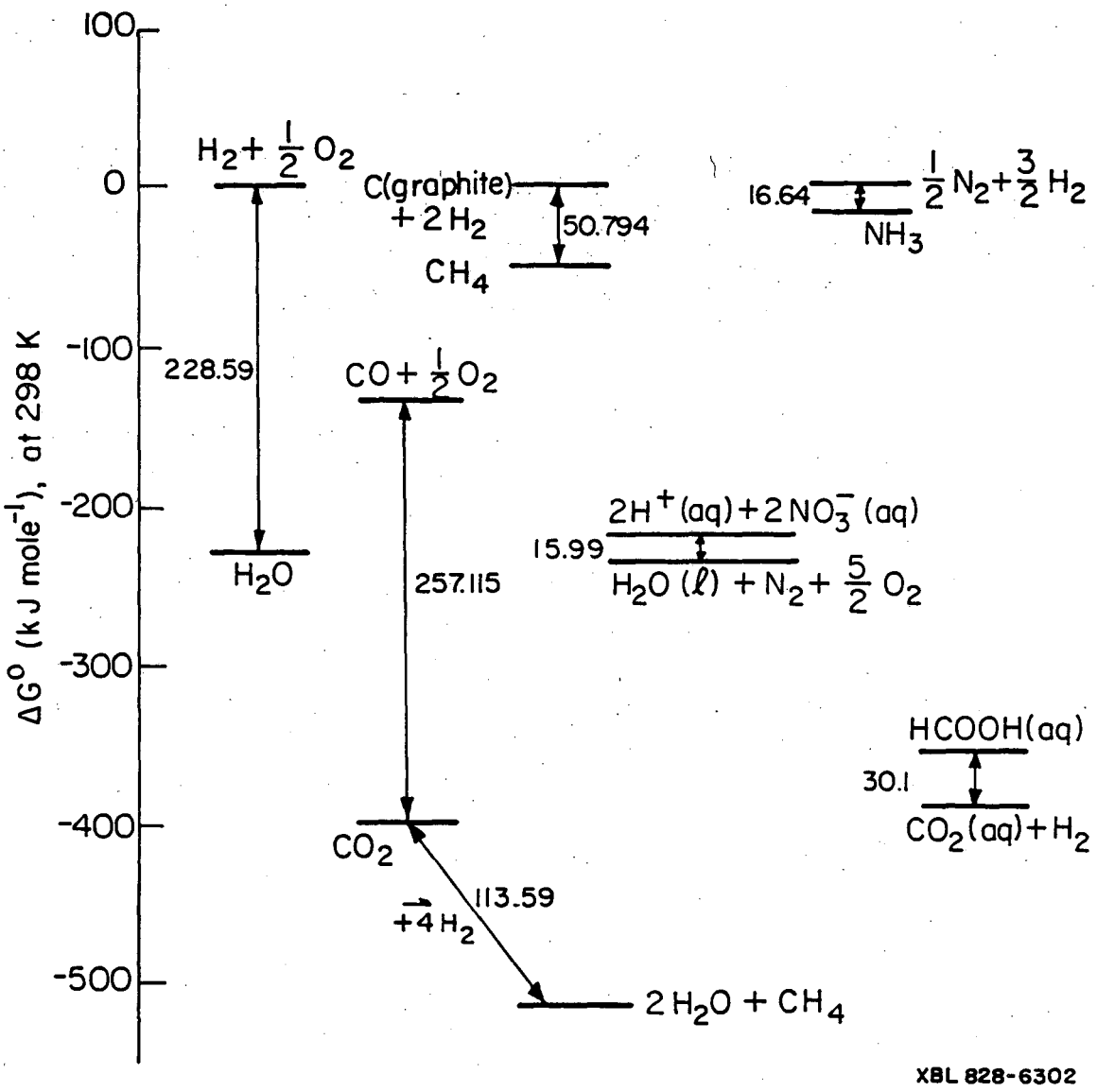

100
0
-100
-200
-300
-400
-500
ΔG° (kJ mole⁻¹), at 298 K
H2 + 1/2 O2
228.59
H2O
C(graphite) + 2 H2
50.794
CH4
CO + 1/2 O2
257.115
CO2
+4 H2
113.59
2 H2O + CH4
16.64
1/2 N2 + 3/2 H2
NH3
2H+(aq) + 2 NO3−(aq)
15.99
H2O (ℓ) + N2 + 5/2 O2
HCOOH(aq)
30.1
CO2(aq) + H2
XBL 828-6302

Fig. 20

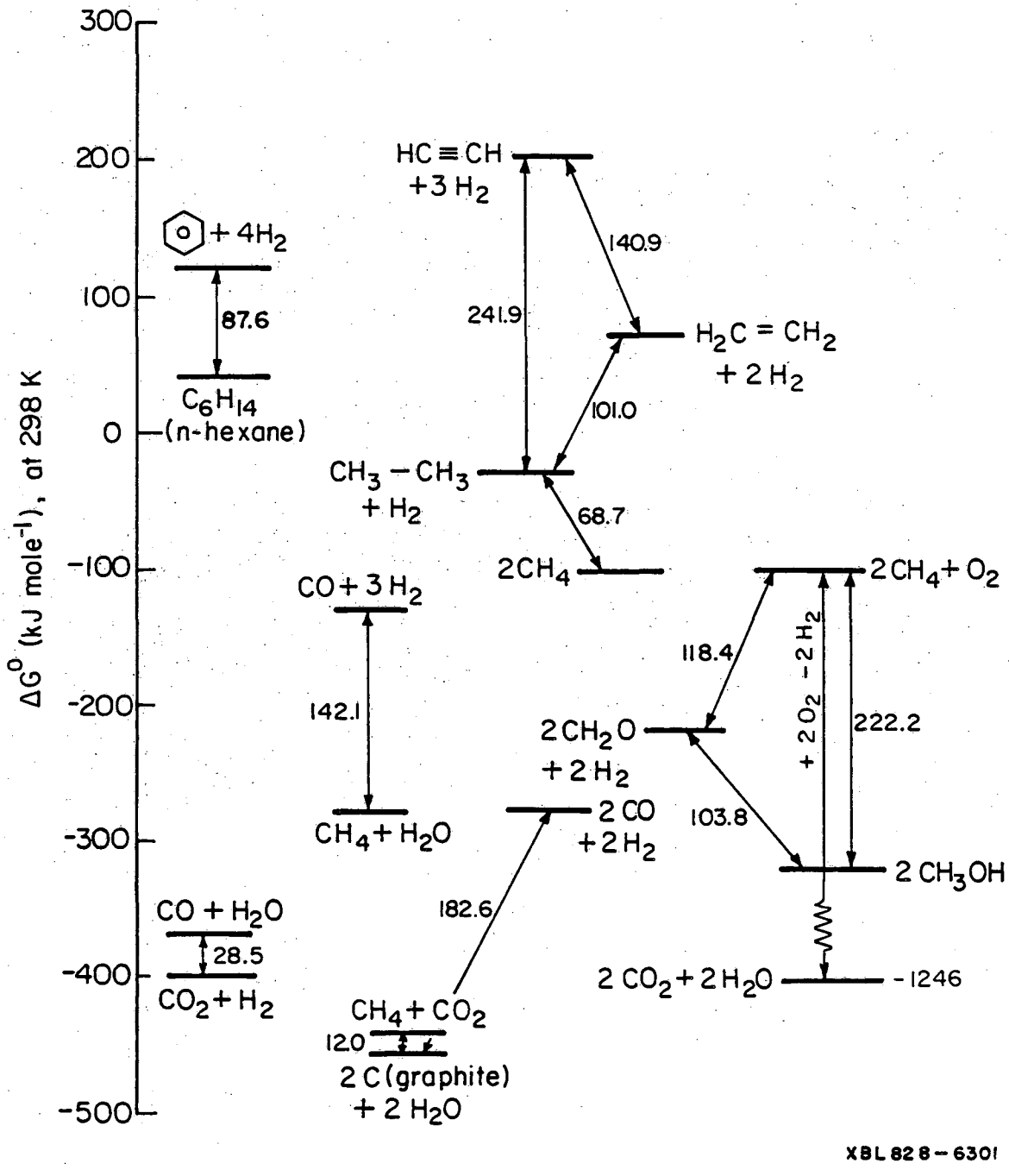

300
200
100
0
-100
-200
-300
-400
-500
ΔG° (kJ mole⁻¹), at 298 K
+ 4H2
87.6
C6H14
(n-hexane)
CO + H2O
28.5
CO2 + H2
HC ≡ CH
+3 H2
140.9
241.9
H2C = CH2
+ 2 H2
101.0
CH3 − CH3
+ H2
68.7
2CH4
CO + 3 H2
142.1
CH4 + H2O
2 CH2O
+ 2 H2
2 CO
+2 H2
182.6
CH4 + CO2
12.0
2 C (graphite)
+ 2 H2O
2CH4 + O2
118.4
+ 2 O2 − 2 H2
222.2
103.8
2 CH3OH
2 CO2 + 2 H2O
-1246
XBL 828-6301

Fig. 21

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