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REPORT OF THE SURFACE SCIENCE WORKSHOP

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REPORT OF THE SURFACE SCIENCE WORKSHOP

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Sponsored by the Materials Science Program of the
Division of Physical Research,
Energy Research and Development Administration

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Research and Development Administration.

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- K. Taylor, General Motors Technical Center
- F. Vook, Sandia Laboratories
- J. B. Wagner, Arizona State University
- G. K. Wehner, University of Minnesota
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- M. Wrighton, Massachusetts Institute of Technology
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INTRODUCTION

A three-day workshop on surface science sponsored by the Materials Science Program of the Division of Physical Research (DPR), Energy Research and Development Administration, was held in Berkeley, March 16-18, 1977, at the Materials and Molecular Sciences Division of the Lawrence Berkeley Laboratory. Its purpose was to assess needs and establish priorities in important areas of materials research in the basic energy sciences. The goals of the Workshop were: (1) to review the various areas of energy development and technology in which surface science plays major roles and makes major contributions, and (2) to identify the major surface-science-related problem areas in the fields within ERDA's mission in the fossil, nuclear, fusion, geothermal, and solar energy technologies and in the field of environmental control.

The meeting was attended by 46 scientists representing industry, academic institutions, and national laboratories. The Materials Science Program office of DPR was represented by Dr. William Clinton, Dr. Robert Epple, and Dr. Stanley Wolf.

The subjects that were discussed in the general area of surface science were as follows:

- Activation of Surfaces
 - A. Catalysis and chemisorption
 - B. Semiconductors, thin films, solar device surfaces
 - C. Electrodes, electrocatalysis, photon-assisted surface reactions
- Passivation of Surfaces
 - D. Corrosion
 - E. Interaction of ions with surface and near-surface regions
 - F. Grain, phase boundaries and interfacial boundaries

The program of the three day Workshop was as follows:

PROGRAM OF THE SURFACE SCIENCE WORKSHOP

Wednesday, March 16 Chairman: G. A. Somorjai

- 9-10 a.m. Nuclear energy conversion and its surface science related problems
Carlos Colmenares, Lawrence Livermore Laboratory
- 10-11 a.m. Fossil energy conversion
Catalysis--Harold Beuther, Gulf Research and Development
Corrosion Problems--Roger Staehle, Ohio State University
- 11-12 a.m. Thermonuclear fusion: the role of surface science
Walter Bauer, Sandia Laboratories, Livermore
- 2-3 p.m. The control of air pollution: the role of surface science and catalysis science
Kathleen Taylor, General Motors Technical Center
- 3-4 p.m. Geothermal energy conversion and surface science related problems
John Apps, Lawrence Berkeley Laboratory
- 4-4:30 p.m. Solar energy conversion: Photovoltaic
Richard Bube, Stanford University
- 4:30-5 p.m. Photochemical energy conversion
Mark Wrighton, Massachusetts Institute of Technology

Thursday, March 17 Chairman: J. T. Yates, Jr.

- 8:30-9:25 a.m. The theory of surfaces: the state of the art
G. Painter, Oak Ridge National Laboratory
- 9:25-10:20 a.m. The atomic structure of surfaces
F. Jona, State University of New York, Stony Brook
- 10:20-11:15 a.m. The electronic structure of surfaces
David A. Shirley, Lawrence Berkeley Laboratory
- 11:15-12:10 a.m. The composition of surfaces
J. Burton, Exxon Research and Engineering Co.
- 1-2 p.m. The dynamics of neutral atoms and molecules at surfaces
Robert Madix, Stanford University
- 2-3 p.m. The dynamics of ions at surfaces
G. Wehner, University of Minnesota, Minneapolis

3-3:30 p.m. Solid-solid and solid-liquid boundaries
D. Maddox, Sandia Laboratories, Albuquerque

3:30-5 p.m. Workshop Activities
Chairman: W. Clinton

Friday, March 18

9 a.m.-4 p.m. Workshop activities

DISCUSSION GROUPS

Activation of Surfaces

A. Catalysis and chemisorption

Theodore E. Madey, Chairman
H. Beuther, R. Eischens, W. P. Ellis, R. Hansen,
R. Madix, G. Painter, A. Perrotta, D. Shirley,
J. Strozier, K. Taylor

B. Semiconductors, thin films, solar device surfaces

Homer Hagstrum, Chairman
J. Gadzuk, R. Eube, J. Galt, G. Cummings, F. Jona

C. Electrodes, electrocatalysis, photon-assisted surface reactions

E. Yeager, Chairman
P. Epple, W. A. Goddard III, P. Stonehart, J. B. Wagner, M. Wrighton

Passivation of Surfaces

D. Corrosion

R. Staehle, Chairman
J. Apps, J. Blakely, A. Frederikse, D. Michels,
J. Morris, Jr., P. Palmberg, J. Rowley, S. Wolf

E. Interaction of ions with surface and near-surface regions

J. Mayer, Chairman
D. Green, F. Vook, W. Bauer, G. Wehner, C. Colmenares

F. Grain, phase boundaries and interfacial boundaries

C. McMahon, Chairman
M. Brodsky, J. Burton, J. Houston, J. Jenkins, D. Maddox,
D. Stein

At the request of the organizers, all of the talks presented overviews of surface science and the various surface-science-related problems of energy technology. During the first day, various energy technology areas were reviewed by experts working in the field, and surface-related problems were exposed and discussed, along with their role in development and technology applications. During the second day the present state of understanding in a number of areas of surface science was discussed. These were also presented as broad reviews by active practitioners working in the respective fields of surface science. The purpose of these lectures was to provide the participants with a broad review of modern surface science and to expose the surface-science-related problems of the energy technologies. After this exposure to surface science and energy technologies the actual Workshop activities began later in the afternoon of the second day and continued through an entire third day. The participants were divided into the six study groups listed above.

The organizers provided the study groups with a series of questions to help focus the discussions. The discussions on these questions were by no means binding. Participants in the study groups were asked to consider all important areas of research and development in their broad field of responsibility. Questions asked of the study groups were organized into two topics: the first topic was aimed at reviewing the state of surface science as related to energy technologies, its role in contributing to data base and to solving problems of existing and new technologies; the second topic was aimed at assessing the

various surface science directions and goals for the future. These questions are listed below.

QUESTIONS ADDRESSED BY THE STUDY GROUPS

- TOPIC 1. The state of surface science as related to energy technologies, its role in contributing to data base and to solving problems of existing and new technologies.
- 1.1. The various fields of ERDA's mission include energy conservation, fossil, nuclear fusion, geothermal and solar energy technologies and environmental control. Identify the fields where most of the surface science problems are concentrated.
 - 1.2. Enumerate the various energy technology problems that may be solved by surface science research.
 - 1.3. Identify, if possible, the long-range surface science research problems where much effort should be concentrated.
 - 1.4. Which are those areas of surface science that are neglected although research in these areas would be important in support of one or several of the energy technologies?
 - 1.5. What sort of physical-chemical data are missing in the field of surface science that would help develop new technologies or better control existing technologies?
 - 1.6. What classes of surfaces need to be better understood at the basic level in order to assure better control of surface processes? What sort of material or process characterization is needed to help develop new technologies or better control existing technologies?
 - 1.7. What theoretical research technique offers the most promise for actual predictive power?
 - 1.8. Describe the experimental techniques and the type of instrumentation needed to obtain the necessary surface science data or surface characterization.
- TOPIC 2. Surface science directions and goals .
- 2.1. Select several highest priority research areas which should be supported in the near future: rank these if possible.
 - 2.2. How would you organize the surface science research so that it has maximum impact on the various energy technologies? How would you optimize the research development technology information flow?

- 2.3. What do you consider as the critical mass of research groups in surface science to provide the necessary basic materials and process control information in your area of concern? Do we have this critical mass?
- 2.4. What are the major obstacles in the way of developing close cooperation between national laboratories and industry? How could these obstacles be best removed?
- 2.5. Are there important areas of surface science research that impact on energy technology where the best work is carried on outside the United States? Please indicate where.
- 2.6. (a) How would you provide a mechanism to educate technical personnel for employment in the various energy technologies?
 (b) How would you provide a mechanism to retrain technical personnel already working in the energy technology fields, in modern surface science?

There were general conclusions and recommendations common to all of the study groups. These are summarized below. The specific highest priority recommendations applicable to the six specific areas of surface science are listed after the general recommendations.

Detailed recommendations of each of the study groups are reported in the Appendix.

WORKSHOP PRIORITIES

1. THE ORGANIZATION OF SURFACE SCIENCE RESEARCH

Surface Phenomena--A Pervasive Area in the Energy Sciences

From the very large number of specific examples discussed in this study, it is clear that surface phenomena play a dominant and widespread role in the various energy technologies. Our ability to tailor-make surfaces having desirable physical and chemical properties will be a major controlling factor in our future efforts to achieve energy conversion and energy conservation over the wide range of energy technologies. Basic research on surface phenomena, therefore, should

yield concepts and data which will have a broad impact on our future ability to generate, convert, and store energy.

A Major Commitment to Long-Term Research Programs

There was a particular concern among the participants that much of the current funding in energy research areas could go into solving short-term problems, while the most important surface-related problems in most energy areas leading to new directions in energy technology are of a long-term nature. Although recurring energy crises always focus attention on short-term difficulties, long-term basic research must be carried out to increase our basic understanding of surface processes and materials. This long-term basic research approach should be a major component in the U. S. energy research effort.

Correlate Molecular and Macroscopic Properties of Materials

Through surface science, we gain a better understanding of the correlation between the molecular surface properties and macroscopic properties of materials. The atomic and electronic surface structures, surface composition and valency, and rates of elementary surface processes (diffusion, adsorption, reactions) should be related to the behavior of surfaces in catalysis, corrosion, grain boundary fracture, embrittlement, radiation damage, adhesion, and lubrication.

Expansion of Research at Interfaces

Surface science research should be broadened to include more studies of interfaces which are of practical importance. Future emphasis should be given to understanding surface processes at interfaces involving condensed phases (solid-solid and solid-liquid). Overlayers of great thickness compared to monolayer dimensions should be investigated

over their entire range of growth. Thick-layer phenomena are of importance in corrosion, ion-surface interactions, electronic devices and boundary problems.

Improvement of Surface Measurement Capability--A Major Need

The development of new surface measurement techniques is a major need within the field. In addition, the calibration of existing techniques such as Auger spectroscopy, ESCA and sputter depth profiling poses major unsolved problems. Incentives should be provided for the invention of new techniques. When necessary, national facilities should be established to carry out surface research involving expensive apparatus.

National Centers for Surface Science Research

Even without coordinated national commitment to surface science research, the U. S. appears to have a leading position in most areas of the field. However, as a result of well-organized national programs in other countries (i.e., U.S.S.R., France, Germany and Japan), the U.S. leadership role may be unlikely to continue in many subareas of surface science. It appears that making a national commitment through the establishment of surface science research centers could be of great value at present. These centers should be designed to foster effective communication between engineers and scientists who have common interests in solving surface problems and to provide access to expensive surface characterization facilities.

Education Within the Field of Surface Science

Training and retraining of U.S. scientists and engineers should have first priority in this rapidly moving field of science. Centers

of research in surface science should provide education and training and exchange opportunities for personnel working in various energy technologies.

Improvement of Communications Between Scientists

The communication between basic research, development, and technology needs considerable improvement. Exchange programs between personnel in national laboratories, industrial laboratories, and academic institutions could improve this situation. Incentives should be provided for research by two or more investigators from various backgrounds (for example, materials science and chemistry, etc.) to carry out joint interdisciplinary research. All areas of surface science that are related to the energy mission would appear to benefit by an interdisciplinary approach.

2. RESEARCH COMMON TO ALL AREAS OF SURFACE SCIENCE

These represent general areas where investment of research funding could have the widest impact on surface and its relation to various energy technologies.

- Studies of reaction dynamics and elementary processes (adsorption, diffusion, bonding and desorption) at surfaces, and related theoretical developments.
- Characterization of structural and electronic properties of surfaces and their influence on surface behavior.
- Study of surface modifiers: poisons, promoters, inhibitors, implanted species. Structural and chemical stabilization of surfaces.
- Surface defect characterization.
- Film growth studies (condensation, growth and evaporation).

- Development of instrumental methods for studies of external and internal surfaces under operating conditions.
- Measurement of sputtering yields and quantification of their surface measurement techniques.
- Surface studies of oxides, carbides, and sulfides.
- Studies of surface properties of new classes of materials: bimetallic clusters, composites, ceramics, polymers, ion implanted materials, intercalation compounds, etc.
- Search for substitutes for precious metals and other surface active materials that are not available in the U.S.
- Studies of the structure, composition and electronic properties of interfaces between condensed media (solid-solid, solid-liquid) and of grain boundaries, and related theoretical developments.
- Strength of interfaces: adhesion, lubrication, grain boundary cohesion, influence of environment.

3. RESEARCH RELATED ONLY TO SPECIFIC AREAS OF SURFACE SCIENCE

Catalysis and Chemisorption

- Development of chemical and physical probes of catalytic intermediates; characterization of active species in catalysis and chemisorption.
- Study of interactions of excited molecules with surfaces.

Semiconductors, Thin Films, Solar Device Surfaces

- Understanding and learning to control the nature of surface states at a free surface, and interface states at metal-semiconductor and semiconductor-semiconductor junctions.

- Study the effect of the structure and chemical composition of grain boundaries on the electrical properties.

Electrodes, Electrocatalysis, Photon-Assisted Surface Reactions

- Study of photon-assisted surface reactions.
- Study of hydrogen and oxygen electrocatalysis.

Corrosion

- Study of ion and ion-base alloy surfaces in the corrosion environments of hydrogen, sulfur, oxygen and water.
- Study of Al_2O_3 , SiN-SiC and other ceramic surfaces in the corrosive environments of hydrogen, sulfur, oxygen and water.

Interaction of Ions with Surface and Near-Surface Regions

- Simulation of radiation damage by study of low-energy ion interactions with surfaces (charge states, charge exchange, photon emission and sputtering yields).
- Study of surface and near-surface modification under ion bombardment conditions (composition, topology, microstructure).
- Studies of surface passivation against radiation damage.

Grain, Phase Boundaries and Interfacial Boundaries

- Experimental and theoretical studies of correlation between free surfaces and grain boundaries with respect to segregation, diffusion, structure and two-dimensional phase equilibria.
- Determination of grain boundary and interface structure, atomic arrangements and defect structure.

APPENDIX: DETAILED RECOMMENDATIONS OF THE STUDY GROUPS

● ACTIVATION OF SURFACES

A. Catalysis and Chemisorption

Theodore E. Madey, Chairman	G. Painter
National Bureau of Standards	Oak Ridge National Laboratory
H. Beuther	A. Perrotta
Gulf Research and Development	ERDA, Pittsburgh Energy Res. Center
R. Eischens	D. Shirley
Texaco Incorporated	Lawrence Berkeley Laboratory
W. P. Ellis	J. Strozier
Los Alamos Scientific Lab.	Brookhaven National Laboratory
R. Hansen	K. Taylor
Ames Laboratory	General Motors Tech. Center
R. Madix	
Stanford University	

In addition to answering the preceding questions, a general concern was voiced concerning DPR's role in research funding. The primary concern of DPR in the areas of catalysis and chemisorption should be the potential for increasing our basic understanding of surface processes. Relevance to energy-related problems is important and should also be of concern. Where appropriate, DPR should take the initiative in establishing joint programs with applied divisions of ERDA, viewing mission-oriented research as support for applied areas, in order to widen the funding basis for basic research. Since industrial support for basic research has dwindled, DPR has a special function to encourage basic research in the overall energy effort. DPR should sponsor a small number of technologists in government to spend some time in universities learning some of the advanced experimental techniques that can be applied to catalytic and materials research in energy programs.

Question I-1: The various fields of ERDA's mission include energy conservation, fossil, nuclear fission, geothermal and solar energy technologies and environmental control. Identify the fields where most of the surface science problems are concentrated.

Answer: Most catalysis and chemisorption problems are concentrated in fossil and fusion technologies and in environmental control, with solar and energy conservation (through efficient energy conversion process) second in importance.

Question I-2: Enumerate the various energy technology problems that may be solved by surface science research.

Answer: Energy technology problems and needs are listed in priorities:

S = short-range goals, L = long-range goals.

A. Fossil

Syn gas ($H_2 + CO$) processing problems:

- 1) Reduction of purification cost, particularly S removal; development of S-resistant catalysts (S).
- 2) Use of surface science tools in analyzing catalyst failure i characterizing differences between successful and unsuccessful catalysts (S).
- 3) Development of catalysts with high selectivity for synthesis of higher molecular weight hydrocarbons and alcohols (L).
- 4) Detection and processing of carcinogenic by-products (L).

B. Fusion and Fission

- 1) Chemisorption on heavily ion-bombarded surfaces (S).
- 2) Hot atom chemistry, particularly on carbon surfaces (S).

3) Development of catalysts for conversion (via shift)

$\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2 \text{O}_2$: development of a closed thermodynamic cycle using heat from nuclear reactions to run a 4- or 5-step H_2 generation cycle (L).

4) Chemisorption in intense radiation fields (L).

5) Ferritics corrosion (L).

C. Solar

1) Chemisorption and external corrosion associated with solar device surfaces (S).

2) Dynamics of growth and synthesis of photoactive surfaces via gas/solid deposition processes under well-defined conditions (CVD) (L).

3) Hydrogen production from H_2O via photocatalysis involving such compounds as TiO_2 and SrTiO_3 (L).

D. Environmental Control

1) Adsorbents and catalysts for stack gas cleanup of coal combustion gases (e.g., SO_2) should be regenerable. NO_x adsorption and reduction (S).

2) Materials substitutes, e.g., for Pt, Pd, and Rh in 3-way auto exhaust catalysts (S,L).

3) Chemistry on particulates and particulate characterization.

4) Catalytic combustion (L).

E. General problems impacting on fossil, fission, and environmental controls: influences of adsorbed C, O, N, S on surface dynamics such as

1) H adsorption, dissociation, permeation;

2) interactions of H_2O and O_2 ; and

3) and catalytic activity as exemplified in

--coke formation and S resistance,

--action of surface "modifiers" such as poisons and promoters.

Question I-3: Identify, if possible, the long-range surface science research problems where much effort should be concentrated.

Answer: Long-term surface science research problems: H = highest priority, L = lower priority.

- 1) Reaction dynamics on well-characterized surfaces; elucidation of the basic steps in surface reaction adsorption in gas-solid interactions along with related theoretical developments and interaction of excited molecules with surfaces (H).
- 2) Development of instrumentation to study catalysts and other well-characterized surfaces under (or applicable to) ambient conditions. Examples include but are not limited to (a) optical and acoustical spectroscopic techniques, (b) neutron scattering, (c) high energy electron microscopy (H).
- 3) Characterization of surface geometric, electronic, and bonding structure--theoretical as well as experimental (H).
- 4) Chemical and physical probes of catalytic intermediates; characterization of the active species in catalysis and corrosion (H).
- 5) Development of alternatives to precious metal catalysts; search for unsuspected activity in well-known materials (L).

- 6) Physics and chemistry of small particles: sintering, particle-support interactions and their influence on reactivity; chemistry on airborne particulates (L).
- 7) Structure and catalytic properties of small crystals and metal clusters (L).
- 8) Studies of highly exothermic reactions; search for better catalyst stability (L).
- 9) Surface thermodynamics of gas/surface systems (L).

Question I-5: What sort of physical-chemical data are missing in the field of surface science that would help develop new technologies or better control existing technologies?

Answer: Physical-chemical data:

- 1) rate constants for elementary reactions on surfaces;
- 2) bond lengths and bond strengths of adsorbed species;
- 3) surface interaction energies, heats of adsorption;
- 4) surface adsorbate densities.

Question I-6: What classes of surfaces need to be better understood at the basic level in order to assure better control of surface processes? What sort of material or process characterization is needed to help develop new technologies or better control existing technologies?

Answer: Research on well-characterized surfaces of the following classes of materials is imperative:

- 1) alloys and mixed metals;
- 2) semiconductors and insulators--oxides, sulfides, carbides;
- 3) amorphous materials.

Question I-7: What theoretical research technique offers the most promise for actual predictive power?

Answer: Theoretical needs include:

- 1) determination of surface electronic structure;
- 2) surface geometry and energetics of adsorption;
- 3) description of dynamic processes such as breaking and formation of bonds at surfaces.

Question I-8: Describe the experimental techniques and the type of instrumentation needed to obtain the necessary surface science data or surface characterization.

Answer: Needed instrumentation: Beyond the necessity of capital equipment expenditures for modernization and development of new surface instrumentation, we support the concept of national facilities or centers to support major efforts in

- 1) surface structure determination, and
- 2) synchrotron radiation. This facility should permit a full range of UPS, XPS, and other surface science measurements. Funds for travel to and experimental set-ups at these facilities should also be provided.

Question II-1: Select several highest priority research areas which should be supported in the near future: rank these if possible.

Answer: Highest priority research areas are listed under Question I-3.

Question II-2: How would you organize the surface science research so that it has maximum impact on the various energy technologies? How would you optimize the research development technology information flow?

- Answer: 1) Impact of surface science research on energy technologies: refer to listing in Question I-2.
- 2) Optimization of information flow:

- a) sponsor international and national meetings and workshops of a topical nature;
- b) encourage a personnel fellowship program for industrial-national laboratory-university exchange.

Question II-3: What do you consider as the critical mass of research groups in surface science to provide the necessary basic materials and process control information in your area of concern? Do we have this critical mass?

Answer: Critical mass question not addressed.

Question II-4: What are the major obstacles in the way of developing close cooperation between national laboratories and industry? How could these obstacles be best removed?

Answer: Major obstacle: proprietary nature of the catalyst industry.

Perhaps catalysts could be used with an agreement not to analyze catalyst composition.

Question II-5: Are there important areas of surface science research that impact on energy technology where the best work is carried on outside the United States? Please indicate where.

Answer: Major areas in which excellent work is done outside of the U. S.: a German surface physics and chemistry "putsch" is occurring in Jülich, Munich, and Garching. It should also be noted that major catalysis institutes in France (Lyon), Japan (Hokkaido), and Russia (Novosibirsk) represent national commitments to catalysis which the U. S. has not undertaken.

Question II-6: (a) How would you provide a mechanism to educate technical personnel for employment in the various energy technologies?
 (b) How would you provide a mechanism to retrain technical personnel already working in the energy technology fields, in modern surface science?

Answer: ERDA-sponsored retraining fellowship program.

E. Semiconductors, Thin Films, Solar Device Surfaces

Homer Hagstrum, Chairman	J. Gadzuk
Bell Laboratories	National Bureau of Standards
R. Bube	J. Galt
Stanford University	Sandia Laboratories
G. Cummings	F. Jona
Calif. Inst. of Tech.	State Univ. of New York

Question I-1: The various fields of ERDA's mission include energy conservation, fossil, nuclear fusion, geothermal and solar energy technologies and environmental control. Identify the fields where most of the surface science problems are concentrated.

Answer: Semiconductor and thin films are most important to ERDA's mission in the field of solar energy (solar photovoltaics in particular). Photovoltaic cells, metallization films, and protective films are also involved.

Questions I-2 and I-3: Enumerate the various energy technology problems that may be solved by surface science research. Identify, if possible, the long-range surface science research problems where much effort should be concentrated.

Answer: Problems involving solar energy technology may be divided into areas involving solar thermal applications; there is a need for absorbing surfaces that are environmentally stable.

Photoelectrochemical applications involve primarily a choice of a stable semiconductor system that will permit the photoelectrolysis of water with the production of hydrogen and oxygen.

Photovoltaics are concerned with the direct conversion of solar energy to electricity, using homojunctions, heterojunctions, and metal-semiconductor Schottky junctions. Research is directed at maximizing the open-circuit voltage, quantum efficiency, short-circuit current, fill factor and

solar efficiency, while minimizing recombination losses and reverse saturation current. Photovoltaics may be separated into two categories: those that use single-crystal cells (presumably of Si or GaAs) with concentration of the solar radiation, and those that use thin-film cells in large-area flat-plate form without concentration.

Particular problems associated with concentration involve reflecting surfaces for solar concentrators and specific effects caused by the high-intensity radiation associated with concentration of the sunlight. In this latter category are problems associated with the adhesion of the metallization electrodes and the production of defects in the photovoltaic materials. Simulated high-intensity irradiation using lasers may be useful in understanding and guiding the radiation damage found for highly concentrated solar radiation.

General problem areas related to photovoltaics may be summarized as follows:

- 1) Thin films with particular properties are needed. These include coatings that are anti-reflective, chemically passivating, abrasion resistant, transparent conducting and hermetically sealing.

- 2) Understanding and learning to control the nature of surface states as these manifest themselves in several different ways.

- (a) Surface states at a free surface, their effect on carrier loss through recombination, and the effect of thin

films, chemical treatment, and environment on the identity, character, and properties of these surface states.

(b) Interface states that occur at the interface between two different types of material: metal-semiconductor and semiconductor-semiconductor junctions. Information needs to be sought on the structure of these interfaces and the dependence of interface states on preparation conditions and chemical treatment. The relationship of interface states to interface recombination should also be studied.

(c) Grain-boundary effects that occur within polycrystalline layers or films. Information needs to be sought on the structure of these grain boundaries, their effect on bulk properties, and ways of altering the properties of these grain boundaries through diffusion or segregation of deliberately chosen impurities.

(d) Metal-semiconductor interfaces are significant not only because of the role of Schottky barriers in photo-voltaics, but also because of the importance of low-resistance contacts to junction semiconductors. The importance of such low-resistance contacts is accentuated in high-current-density applications such as that involving concentration of sunlight.

Question I-4: Which are those areas of surface science that are neglected although research in these areas would be important in support of one or several of the energy technologies?

Answer: The most important areas of surface science that need added emphasis in order to support solar energy technology are the following:

1) Studies of the effect of intense long-term irradiation by light in the solar spectral region on semiconductor-metal interfaces and as a means of defect production in the surface or near-surface region of semiconductors.

2) Interface studies. This refers to solid-solid and solid-liquid interfaces. There is a need for chemical and atomic structure as well as electronic structure information at these interfaces. The interfaces referred to here include grain boundaries and heterojunctions, as well as metal-semiconductor and liquid-semiconductor interfaces. Some of these are coherent, and some incoherent.

3) Studies of the relation between the properties of the interfaces in 2) to the electrical properties of a structure.

4) Crystal and thin-film growth processes and the resulting kinetics on amorphous as well as crystalline substrates.

Question I-5: What sort of physical-chemical data are missing in the field of surface science that would help to develop new technologies or better control existing technologies?

Answer: We do not suggest that funds be awarded for the specific purpose of collecting and organizing physical-chemical data, but we believe that tabulation of selected properties of

materials could be useful to groups in the development and basic research areas. For example, ionization cross sections and back-scattering profiles of the elements under different excitation conditions would be useful to the person trying to quantify information from AES spectra; sputtering yields of materials as functions of ion energies would be helpful to surface scientists, thin film growers, etc.; data on epitaxial systems, i.e., temperature, rates, orientations, etc. for single-crystal growth would be valuable to the device-fabrication people and so would the compilation of surface recombination velocities in well-characterized materials.

Question I-6: What classes of surfaces need to be better understood at the basic level in order to assure better control of surface processes? What sort of material or process characterization is needed to help develop new technologies or better control existing technologies?

Answer: The "ordered" interfaces normally encountered in epitaxially grown layers need detailed characterization to assist and control the impact on technology uses, such as photovoltaics. Similar considerations apply to semiconductor-metal interfaces to assure good electrical conductivity with high reliability.

To the extent that grain boundaries can be considered as surfaces, the impact on bulk electrical and transport properties needs to be defined carefully. These questions can be addressed only by a thorough understanding of the structural, electrical, optical, etc. properties of the surface itself. Further, control of these properties by selected treatments needs to be defined and developed.

Segregation to and diffusion of impurities along grain boundaries are process variables which are surface related and require careful characterization. Studies should be directed at both the use and control of process results.

Question I-7: What theoretical research technique offers the most promise for actual predictive power?

Answer: A complete quantum chemical theory of semiconductor and thin-film properties seems most unlikely, particularly when one considers the primitive predictive state of theories of even the simplest gas phase atom-diatomic molecule interactions. It thus seems unrealistic to expect that theorists will produce first-principle theories with reliable predictive powers, at least with regard to energy technology problems. Where then lies the role of theory?

We suggest the following possibilities. First-principle theories should be constructed on a few well-chosen systems that can be checked against carefully controlled idealized laboratory experiments. Having established the essential correctness of these theories, semi-empirical extrapolations of these theories into more tractable forms could be made. With these simpler forms of the theories, predictions of macroscopic material behavior, based on microscopic considerations, would be possible. In essence, the insight gained by a few large and idealized calculations will lead to the formulation of some "Pauling-type" rules for surfaces. In order for such a development to occur, a data base of relevant physical quantities is necessary, since trends in

theoretical generalizations are more likely to come from data than from extensive computations.

Question I-8: Describe the experimental techniques and the type of instrumentation needed to obtain the necessary surface science data or surface characterization.

Answer: In the area of semiconductors, films, and solar devices, new experimental techniques are required to investigate and characterize all sorts of interfaces, such as those that occur between metals, between metals and semiconductors, between semiconductors and semiconductors, at grain boundaries, and at defects. Most surface science instrumentation at present is suited to the study of the vacuum-solid interface. To look at internal interfaces new techniques might be devised in which atoms present or introduced into the interface are used as probes from which electrons are excited by radiation or in Auger processes. Such electron spectroscopy of these implanted atoms would yield information on the local chemical and electronic environment. Other possible experimental approaches to obtaining the necessary surface science data are ion channeling and backscattering, Auger spectroscopy with ion milling, and ion desorption spectroscopy.

In developing new experimental techniques, problems arise in which theoretical clarification and understanding of the measurement process is essential in order to separate measurement artifacts from data relating to the system properties.

Close cooperation and collaboration between experimenters and theorists is quite essential in this phase of surface research.

Question II-1: Select several highest priority research areas which should be supported in the near future: rank these if possible.

Answer: The most significant area of future research involves the characterization of interfaces and grain boundaries. Such a characterization should include the structural, electrical, chemical, and metallurgical properties of the interface or grain surface. Furthermore, it should include only such information as this on the property of the interface itself, but also on the effects of the existence and functioning of such an interface on the surrounding bulk. Metal-semiconductor and semiconductor-semiconductor interfaces should be added to the presently investigated metal-metal interfaces in order to enhance relevance to the energy program.

A second area of research concerns the determination of the atomic structure of surface and interface defects as well as their electronic structure and the effects of these defects on mechanical properties. Since many of the techniques of surface science have not been extensively compared with one another, it is recommended that multiple investigations of the same property be carried out with different techniques, as well as carrying out multiple types of measurements on the same sample. To date, correlations involving atomic

structure have been weaker in this regard than correlations involving electronic structure. Finally we recommend that particular attention be paid to the quantification of the basic investigative and characterization techniques.

Question II-2: How would you organize the surface science research so that it has maximum impact on the various energy technologies? How would you optimize the research development technology information flow?

Answer: As to the organization of surface science, the following remarks may be made. First, there must be a critical mass in any surface science research group which is to be effective. This may be achieved by cooperation among people from different institutions, but the group should include both theoretical and adequately equipped experimental capability. Second, it is desirable that in at least some cases the same institution should include a research group as well as a development activity in relevant energy technology. This interaction is likely to have a positive effect on both groups. This is also a very important way to optimize the research-development-technology information flow. The research funding agency can improve this information flow further by holding suitably timed topical conferences to which personnel from the different functional groups are invited, and by discussing research results and proposals with the leaders of the technological effort. Efforts to stimulate cooperation between groups rather than simple competition for research funding should be sought.

Question II-3: What do you consider as the critical mass of research groups in surface science to provide the necessary basic materials and process control information in your area of concern? Do we have this critical mass?

Answer: The precise number of people constituting the critical mass in any given group is likely to vary with the specific activity of the group, but in general the coexistence of and the close interaction between experimentalists and theorists is beneficial and often necessary. In most areas a minimum number of people may involve three to four professionals if adequate technical and computational support is available. As for the number of groups working on the same or similar problems in different geographical areas, it is suggested that a minimum of four or five may be the critical number required to sustain interest, create a competitive spirit, and establish the important system of checks and balances that is necessary for progress.

Question II-4: What are the major obstacles in the way of developing close cooperation between national laboratories and industry? How could these obstacles be best removed?

Answer: Major items of concern in fostering cooperation between national laboratories and industry involve scheduling of work and the specific goals of the two institutions. Basic research is a proper activity of a national laboratory, but perhaps areas of investigation should be selected and supported on the basis of a long-term technology strategy. The national laboratories should be part of and responsive to the planning cycles leading to these technology strategies. Items of specific attention in this area might include:

- 1) Emphasis on time phasing of industrial technology needs.
- 2) Maintaining contact with technology development from initial concepts, through to proof of concept and reduction to practice.
- 3) Using laboratories to serve as effective technology demonstration sites to illustrate utility and reliability.
- 4) Using laboratories to serve as test sites for system study efforts.

Question II-5: Are there important areas of surface science research that impact on energy technology where the best work is carried on outside the United States? Please indicate where.

Answer: In general there are few areas outside the U.S. where better work has been done in the area of surface science. Perhaps one area to be singled out is that of high-resolution electron energy loss spectroscopy where considerable work has been done in Germany, although this work leans heavily on original work on high resolution analyzers done at NBS in the U.S. It also appears that the training of researchers in electron microscopy (SEM, TEM) is occurring most strongly outside the U.S., particularly in England.

Equivalent work on photoemission has been done in Germany, on field or photoemission of polarized electrons in Switzerland, and on ISS in Germany.

Most of the relevant semiconductor work done in the USSR, Germany, France, and Japan is heavily toward technological emphasis and away from surface science.

- Question II-6: (a) How would you provide a mechanism to educate technical personnel for employment in the various energy technologies?
(b) How would you provide a mechanism to retrain technical personnel already working in the energy technology fields, in modern surface science?

Answers: The task of educating and/or retraining technical personnel can range from a developing awareness to developing skills. At one extreme, short courses, workshops, and carefully distributed applications reports can do much to promote the role and impact of surface science on the energy technology community. The development of surface science technical skills is an entirely different problem and will probably require an extended association (6 months to 2 years) with a functioning surface science laboratory. Programs similar to the American Vacuum Society's program in vacuum technology might serve as models.

C. Electrodes, Electrocatalysis, and Photon-Assisted Surface Reactions

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Question I-1: The various fields of ERDA's mission include energy conservation, fossil, nuclear fission, geothermal and solar energy technologies and environmental control. Identify the fields where most of the surface science problems are concentrated.

Answer: Electrochemistry represents the direct conversion interface between chemical and electrical energy and as such is of major importance to ERDA's missions in the several areas outlined in Table 1. Electrochemical corrosion has not been included in this table since it is covered by a separate workshop group. Photosynthesis cells which produce fuels such as H_2 or other useful chemicals such as Cl_2 have been included since these systems involve electrochemical processes at surface. The field of photo-assisted surface chemical reaction, however, encompasses areas outside of electrochemistry and will be covered in a separate section.

Several of the areas indicated by asterisks in Table 1 are of particular importance because of the magnitude of their potential impact and the good prospects for their successful development.

Table 1. Relation of electrochemistry to ERDA's mission.

GENERAL DEVICE OR PROCESS	EXAMPLES
I. Energy Conservation	
A. Load leveling, peak shaving in electric power generation	
1. fuel cells	$H_2-CO/H_3PO_4/O_2$ (air)
2. storage batteries	Li(Al)/molten halide/Fe
3. variable load industrial electrolysis cells	variable load chlor-alkali cells
B. Base load electric power generation	
1. fuel cells	H_2-CO molten carbonate O_2 (air)
C. Vehicle propulsion*	
1. storage batteries*	Ni-Zn cells Li(Al) molten carbonate FeS_2 Na $\beta-Al_2O_3$ S $CH_3OH/H_3PO_4/O_2$ (Air)
2. fuel cells	
D. Industrial energy conservation*	
1. industrial electrolysis*	chlor-alkali cells for Cl_2 , NaOH production
2. electrothinning of metals*	Al electrothinning
E. The H_2 economy and related concepts	
1. fuel cells	$H_2/H_3PO_4/O_2$ (air)
2. water electrolyzers	H_2 ROH O_2 †
II. Fossil fuels*	
A. Hybrid power plants involving high-temperature fuel cells*	
	coal gasification $\rightarrow H_2-CO$ molten carbonate $\xrightarrow{\text{heat}}$ turbine
B. Electrochemical synthesis of hydrocarbons, methanol from CO_2	
	$CO_2 + 2H_2O \rightarrow CH_3OH + 3/2 O_2$

*Areas of particular importance because of the magnitude of their impact and good prospects for successful development.

Table 1. Continued.

GENERAL DEVICE OR PROCESS	EXAMPLES
III. Solar energy	
A. Photoelectrochemical cells	
1. photogalvanic cells	$\text{CdTe} \text{Te}^{2-}, \text{Te}_2^{2-} \text{Pt}$
2. photorechargeable cells	three-electrode system third electrode storage function
3. photoproduction of fuels and organic chemicals	$\text{O}_2, \text{SrTiO}_3 \text{KOH} \text{H}_2$ $\text{Cl}_2, \text{SrTiO}_3 \text{NaCl} \text{H}_2$
IV. Environmental control	
A. Alternative electrochemical systems for synthesis and electrothinning (e.g., elemental contaminants such as Hg, asbestos, SO_2, CN^-)	chlor-alkali cells using no asbestos separators or mercury
B. Sewage treatment	chlorate cell $(\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{NaClO}_3)$
C. Electrochemical recovery of metals in industrial wastes	Cu , Zn , Ni
D. Electrochemical sensors	electrodes specific to O_2 , CO , H_2 , various ions

Questions I-2 and I-3: Enumerate the various energy technology problems that may be solved by surface science research. Identify, if possible, the long-range surface science research problems where much effort should be concentrated.

Answers: Table 2 summarizes some of the problems impeding the development and application of various electrochemical systems and the corresponding long-range surface science research needed to help solve these problems.

Many of the technological problems are associated with the electrocatalytic properties of the electrodes, i.e., insufficient catalytic activity, susceptibility to poisoning, loss of electrocatalyst area, and high cost. Electrocatalysis is a part of the larger field of heterogeneous catalysis but enjoys the additional benefits and complications associated with having the potential energy barrier heights for the charge transfer steps controlled by the potential drop across the interface. This potential drop and hence the electrochemical reaction rates can be controlled externally.

In recent years laboratory techniques have been developed for reducing impurities at the interface to a sufficiently low level that they do not interface with the catalysis in a number of electrochemical systems. As a result, electrocatalysis has emerged as a science in the laboratory. In industrial applications, however, electrocatalysis remains still more an art than a science, with impurity effects usually greatly reducing the catalytic activity of the electrode surface. This results in reduced current densities,

Table 2. Energy technology problems and corresponding long-range surface science research in electrochemistry.

I. Fuel cells

A. Moderate temperature cells (~250°C)

1. Problem: to find high-activity, long life, low cost electrocatalysts for anodes operating on practical fuels (e.g., $H_2 + CO$) and oxygen (air) cathodes.

Research: (a) establish a predictive base to guide the identification of new catalysts and the optimization of existing catalysts, (b) develop an understanding of poisoning effects, (c) develop an understanding of morphological changes in high area catalysts.

B. High-temperature molten carbonate cells (~600°C)

1. Problem: to develop porous electrodes* resistant to electrolyte attack and poisoning (including S), maintaining proper electrolyte distribution within the pore structure.

Research: (a) develop understanding of the factors controlling corrosion of metals in molten carbonates, including passivation phenomena, (b) studies of adsorption and growth of oxide and sulfide layers on metals in molten salts, (c) studies of the factors controlling contact angles and electrolyte filming on electrolyte surfaces in molten salts.

2. Problem: to develop stable electrolyte tiles with the molten carbonate immobilized by a dispersed solid phase (e.g., $NaAlO_2$).

Research: interfacial properties of oxides in molten salts (including $NaAlO_2$ in molten carbonates).

*Electrocatalytic activity is much less of a problem in high-temperature fuel cells.

Table 2. Continued.

 II. Storage batteries

A. Aqueous low-temperature cells (e.g., nickel-zinc)

1. Problem: morphological changes at negative electrode (e.g., dendrite formation).

Research: studies of electrocrystallization and electro-dissolution with particular attention to mechanisms, surface mobilities of adatoms and adions, the role of defect structures, and the effects of adsorbed species on the crystal growth.

2. Problem: passivation of the negative electrode at high current densities.

Research: structural and kinetic studies of metal passivation in electrolytes.

3. Problem: to find new positive electrodes affording higher energy densities and better cycle life.

Research: (a) studies of the surface factors controlling the kinetics of electroreduction and electrooxidation of metal oxides, (b) studies of oxygen overpotential on metal oxides.

B. High-temperature molten salt cells, particularly the ERDA Li(Al) molten halide FeS_x cell

1. Problem: morphological changes at the negative electrode (dendrites).

Research: studies of electrocrystallization and electro-dissolution in molten salts (particularly Li and Li alloys in lithium halide melts).

2. Problem: to find stable separator materials for use in molten salts.

Research: general materials research in molten salt media with particular attention to how bulk and surface properties control kinetics of surface attack.

Table 2. Continued.

C. High-temperature solid electrolyte cells, particularly the Na β -Al₂O₃ S cell

1. Problem: morphological changes in the β -Al₂O₃ at the electrode-electrolyte interfaces.*

Research: general studies of electrochemical interfacial properties of metal-solid ionic conductor interfaces, including liquid metals.

III. Industrial electrolysis and metal electrowinning

A. Inorganic chemicals by industrial electrolysis** (e.g., chlor-alkali, fluorine, water electrolysis)

1. Problem: to reduce voltage losses associated with reaction overpotential with low-cost electrodes.

Research: electrocatalysis research (see I.A.1. in this table); electrodes of special interest include H₂, O₂, Cl₂, ClO₃⁻, ClO₄⁻.

2. Problem: to reduce cell voltage through the use of O₂ (air) cathodes in place of H₂ anodes and H₂ anodes in place of O₂ anodes when H₂ is available.

Research: electrocatalysis research (see I.A.1 in this table) on O₂ reduction and H₂ oxidation.

B. Organic electrosynthesis

1. Problem: to develop new electrosynthetic industrial processes which lead to energy conservation and make more effective use of our carbon sources [e.g., synthesis of hydrocarbons, alcohols from CO₂, low-hydrogen fossil fuels (coal, shale oil)].

*The problems at the β -Al₂O₃-S, NaS_x interface are highly specific to this cell and are not particularly conducive to support with longer range more general research.

**Ionic reflective membranes for industrial electrolysis have not been included since the problems are principally associated with the bulk membrane phase.

Table 2. Continued.

C. Metal electrowinning: aqueous solutions (e.g., Cu, Zn, Cd, Co, Ni, Mn)

1. Problem: to reduce cell voltage losses at anodes.

Research: Electrocatalysis research on O₂ generation (see part I.A.1 in this table).

D. Metal electrowinning: molten salts (e.g., Al, Mg, alkali metals)

1. Problem: to reduce cell voltage losses at the anode* in the Hall cells used for Al.

Research: electrokinetic and electrocatalysis studies in molten salts.

IV. Electrochemical sensors for environmental control

1. Problem: to develop further highly specific electrodes.

Research: electrocatalysis with respect to specific species (e.g., O₂, CO, CN⁻).

*Despite the high temperatures, significant reaction overpotential appears to persist at the anode in the Hall cell for the reaction $2O^{2-} + C \rightarrow CO_2 + 2e^-$.

excessive voltage losses (reaction overpotential), higher catalyst loading requirements, shortened electrode life, and undesirable competing reactions. Consequently a major need exists, not only for electrocatalysts of high initial activity but, equally important, high tolerance to impurities in the electrolyte and reactant feeds and long-term stability. Impurity effects are not well understood in electrocatalysis.

The objective of long-range electrocatalysis research is to develop a predictive base for a number of important electrochemical processes (e.g., H_2 , CO, hydrocarbon oxidation; O_2 reduction; H_2 , O_2 , Cl_2 generation). To achieve such requires the identification of reaction pathways (including adsorbed intermediates), the relationship of the adsorption energies to electrode surface properties, solvent interactions with the electrode surface and the potential energy surfaces for the charge and atom transfer steps. A critical ingredient is the close cooperation of the theorist and experimentalist; unfortunately, this ingredient has been missing in most electrocatalysis research.

In fuel cells and many batteries and industrial electrolysis cells, very high electrode surface areas are used to achieve sufficient electrocatalytic activity. These high areas are obtained through the use of highly porous electrocatalytic layers or extremely small catalyst particles on a porous electrode substrate. Morphological changes usually occur with use, however, and these lead to a loss of this high

area. These changes are a severe problem and not well understood.

Most advanced fuel cells, batteries and industrial electrolytic systems present very hostile environments for the electrodes, separators, diaphragms, membranes, and containment materials. The deterioration processes are not well understood and involve much surface chemistry.

Question I-4: Which are those areas of surface science that are neglected although research in these areas would be important in support of one or several of the energy technologies?

Answer: Areas of electrochemical surface science receiving insufficient emphasis:

1. Photon-Assisted Reactions at Surfaces

Photoreactions at surfaces have received little attention, but the possibility of using surfaces to mediate the photochemical (solar) formation of fuels and conversion of light to electricity may have an impact on future energy resources. This emerging research area most concerns ERDA's mission in solar energy. This field presently has no identifiable practical scale energy technologies associated with it, but within the past two years there have been two important laboratory demonstrations of light to chemical and electrical energy conversion by irradiating semiconductor electrodes exposed to liquid electrolytes. In one example, SrTiO₃ (n-type semiconducting) has been shown to efficiently convert ultraviolet light to chemical energy in the form of H₂ and O₂ from the photoelectrolysis of H₂O. Solar energy efficiency was estimated

to be of the order of 1%. N-type CdX (X = S, Se, Te) in electrolytes containing Na₂X have been shown to serve as the photoanode in cells for the conversion of light to electricity with solar efficiency (5-8%) rivaling the values obtained for wholly solid-state devices (photovoltaics). In each case, polycrystalline semiconductors have been shown to work with efficiencies approaching those found for single crystals. These recent discoveries may lead to device applications and presently command a great deal of interest in industrial, academic, and government labs in the U.S. and abroad. Some of these applications and the basic research undergirding their development are outlined in Table 3.

Significant potential exists as well in the use of surfaces in non-electrode applications for photochemical fuel formation. In driving uphill reactions the problem is to build in barriers at each step which precludes back reactions. This is opposite to the goal of catalyst research which is to remove all kinetic barriers to thermodynamically favorable reactions. There is considerable merit in considering that surfaces (semiconductors, chemically modified semiconductors, organic polymers) can serve to photoassist the conversion of raw materials (N₂, O₂, CO₂, H₂O, etc.) to fuels. Promising lines of effort here should involve exploring evaluation of the kinds of photoprocesses that can be carried out on surfaces and with special aims toward establishing unique chemical processes induced by light and a conscious effort to promote energetically

Table 3. Semiconductor photoelectrodes: applications and basic research.

Applications	Basic Research Needed
Photoelectrolytic cells for fuel formation (e.g., $H_2O \rightarrow H_2 + 1/2 O_2$)	1. Study of polycrystalline surface/electrolytic interface vs single crystal.
Cells for converting light to electricity (e.g., CdTe in Na_2Te/Na_2Te_2 electrolyte)	2. Establishment of factors controlling semiconductor photostability.
Photochargeable batteries	3. Elucidation of interface energetics and charge-transfer kinetics.
Photoelectrosynthesis of chemicals	4. Definition of prospects for using electrode catalysts at photo- and counter-electrodes.
	5. Study of surface states.
	6. Mechanisms for electrode sensitization.
	7. Chemically derivatized electrode surfaces for kinetics, stability, wavelength response, specificity, manipulation.
	8. Consequences of light intensity and temperature.
	9. Exploratory photo-induced redox.

uphill reactions (e.g., $\text{CO}_2 \rightarrow \text{CO} + 1/2 \text{O}_2$) with light. The irradiation of surfaces may also serve to generate thermally active catalysts having simultaneously improved activity and selectivity. There is a serious lack of real effort in this area which is, admittedly, just beginning. Theory directed towards the establishment of surface reaction activation energies would be particularly fruitful in pinpointing the nature of the photo process desired. Instrumentation and techniques for the study of photoinduced reactions on surfaces will logically involve those outlined in other appropriate sections of this report.

Looking to the future, it is reasonable to factor fundamental development in the area of photochemistry at surfaces. Exploratory studies of gas-solid and liquid-solid interfaces are appropriate. Moreover, in view of the success with photoelectrodes it is not unreasonable to begin the consideration of scale-up and associated surface science problems. But basic photochemical studies should receive highest priority to clarify the realistic prospects for photochemical energy conversion.

2. Electrocatalysis

Electrocatalysis received considerable attention in a number of industrial laboratories and a few government laboratories in this country in the 1950's and 1960's, principally in conjunction with fuel cell research. Most companies abandoned this work in the late 1960's. Over the past two or three years

there has been evidence of renewed interest in electrocatalysis research in industrial laboratories of companies involved in large-scale electrolysis and electrowinning, principally as a result of escalating electric power costs. Most of the industrial research in electrocatalysis has been quite applied and has not contributed much to the science.

Very little electrocatalysis research has been carried out in academic laboratories in this country, with only two or three physical electrochemists working in this area. Over the past few years, the situation has improved somewhat with several academic electroanalytical* chemists shifting into this area. The importance of the field to our country and the increasing vigor of the science warrant a much greater effort in academic laboratories, enlisting surface physical, inorganic, and organic chemists and theorists as well as experimentalists.

3. The Electrochemistry of Oxides

Oxide films and bulk oxides play an important role as electrocatalysts, reactants in batteries, and passivation layers in corrosion inhibition. Relatively little is known about oxide-electrolyte interfaces. With the exception of passivation films in metals, little fundamental research has been carried out on such interfaces.

*Over the past 40 years, most of the academic research in electrochemistry in the U.S. has been carried out by electroanalytical chemists, who kept the subject alive on university campuses over the years when electrochemistry as a surface science was in too unhealthy a state to attract physical chemists.

4. Electrocrystallization and Electrodisolution

Electrocrystallization and dissolution play an important role in various batteries and industrial electrochemical processes, including electroplating and electromachining. Fundamental surface physics research in this area is almost nil in this country.

Question I-5: What sort of physical-chemical data are missing in the field of surface science that would help develop new technologies or better control existing technologies?

Answer: Supporting physical chemical data which prove useful to electrocatalysis research and for which it is possible to obtain meaningful values with existing methods include the following:

1. Adsorption isotherms, heats of adsorption and electro-sorption valencies for various species at metal-electrolyte interfaces; e.g., H, O, OH⁻, halides, S⁼, CO, CO₂, small organic molecules.
2. Ionic double layer properties of solid electrodes (polycrystalline and where possible, single-crystal surfaces) in aqueous solutions.
3. Standard rate constants and transfer coefficients for the H₂ and O₂ electrode reactions on various well-defined electrode surfaces under ultrapure conditions.
4. Work functions for solid-gas interfaces.
5. Heats of wetting of metals with water.

Question I-6: What classes of surfaces need to be better understood at the basic level in order to assure better control of surface processes? What sort of material or process characterization is needed to help develop new technologies or better control existing technologies?

Answer: The electrochemical interface involves an electronic conductor as the electrode phase in contact with an ionic conductor as the electrolyte phase. A wide assortment of each type of conductor is involved in energy-related technologies, particularly in the electrocatalysis area. Typical electrode phase materials include:

1. pure and alloy metals
2. underpotential deposited monolayers on foreign metal substrates
3. carbon and graphites
4. metal carbides (e.g., WC, NiC)
5. intermetallic compounds (e.g., GaAs)
6. oxides (principally transition metal)
7. sulfides (principally transition metal)
8. transition metal complexes: thin films, monolayers (e.g., transition metal macrocyclics)
9. electronically conducting polymers (e.g., SN_x , polymeric transition metal complexes)
10. elemental semiconductor (e.g., Ge, Si).

In many instances these electrode materials are used in very high-area-forms with high-defect structures. There is much evidence to demonstrate that the defect structure and non-stoichiometry are often important to the catalytic

activity and general electrochemical behavior. The high areas are achieved through the use of highly porous electrodes with much of the pure spectrum often below 10^+3\AA . Typical electrolyte phases include:

1. aqueous electrolytes, including extremely concentrated systems with all water bound to ions (e.g., $\text{KOH}\cdot\text{H}_2\text{O}$, $\text{ZnCl}_2\cdot 4\text{H}_2\text{O}$, 96% H_3PO_4);
2. organic solvents (particularly aprotic);
3. molten salts (particularly halides, carbonates);
4. ionic conducting solids (e.g., $\beta\text{-Al}_2\text{O}_3$, $\text{Ag}_x\text{Ru}_y\text{I}_z$).

The single most generally useful materials characterization for those various combinations of interfaces is the stability of the interface as a function of potential and temperature. The stability is more than just a matter of thermodynamics and equilibrium solubility. In many instances, long-term stability is achieved because of slow kinetics even though the electrode phase has high solubility in the electrolyte.

Question -7: What theoretical research technique offers the most promise for actual predictive power?

Answer: In the explanation, prediction and design of electrochemical and photon-assisted systems, reliable theoretical methods are essential to provide:

- i) heats of chemisorption of various molecules, radicals, and reaction intermediates onto electrode materials;
- ii) structure of chemisorbed molecules;
- iii) reactive surfaces and activation energies for charge and atom transport across solid-liquid interfaces;

- iv) the dependence of the above quantities upon composition and character of the electrode site;
- v) for photo-assisted processes it is particularly important to consider the above quantities for excited states in order to learn where a photon could be used to assist a reaction and where one can get a sizeable potential barrier to prevent back reaction;
- vi) the above quantities would be studied as a function potential difference across the solid-liquid interface;
- vii) involving (iii) and (vi), we would use dynamic techniques to calculate basic rate quantities for atom and charge transfer.

It is important to emphasize that particularly for reaction intermediates the concentrations and lifetimes will be such that only theoretical methods may provide the required data.

In (i) to (vi) the required theoretical techniques are those of electronic structure. For such theoretical studies it is essential to obtain total energies and particularly for (i), (iii), and (v) it is necessary to include the localized electron correlation or moving body effects involved in the bonds undergoing rupture or reaction. Consequently, the suitable methods are generally of the chemically oriented type rather than of the bond-structure-oriented type. (The chemically oriented techniques generally replace the electrode surface with a cluster of atoms and treat the surface adsorbate as a large valence; the bond-structure type calculations

generally model the Hartree-Fock equations, thereby getting photoemission directly, but not total energies.)

Both quantum and classical techniques are being developed and applied to atom and molecular systems and could be applied directly to (vii).

Because of the necessity of total energies the extended Hückel (or tight bonding) type methods will not be suitable. The Hartree-Fock based methods (either ab initio or discrete variational $X\alpha$) may be adequate for (ii), (iv), and (vi). To include electron correlation effects as in (i), (iii) and (v) only the configuration interaction, generalized valence bond and multi-configuration self-consistent field methods are suitable. Even with these methods a great deal of care is required to obtain consistent results.

The adsorption of a reactant or intermediate usually requires the displacement of a solvent molecule or another adsorbed solution phase species from a site, and the energetics of this desorption must also be considered. Fortunately the heat of the solvent interaction with many metals is relatively low although this is not true with non-metallic catalysts. Because of solvent polarization fluctuation terms (similar to those described by R. Marcus of Illinois in his treatment of weakly adiabatic electron transfer electrode reactions and by Dogonadze, Levich and Kutnesov of Moscow in their quantum statistical mechanical treatments of electron and proton transfer at electrode surfaces),

solvent effects may also enter into the theoretical calculations of rate constants for charge and atom transfer steps to or from the solution phase.

Question I-8: Describe the experimental techniques and the type of instrumentation needed to obtain the necessary surface science data or surface characterization.

Answer: Experimental methods and instrumentation for characterization of electrode surfaces:

1. In Situ Techniques

Electrochemical methods often have sensitivity to a small fraction of a monolayer, but they lack the molecular level specificity to identify the chemical nature of the adsorbed species or its interaction with the substrate. In an attempt to obtain such information, a number of electrochemists have turned to in situ ultraviolet-visible internal reflection spectroscopy (both specular and diffuse reflections), ellipsometric spectroscopy and internal reflection spectroscopy using transparent electrodes (usually doped tin oxide). The reflection and ellipsometric spectra carry much information concerning the surface electronic properties of the electrode and their modification by the electric field and adsorbed species. The problem is to extract the information from the spectra. So far, the molecular level information obtained from such studies has been modest. As theorists focus their attention on species adsorbed on metals and semiconductor surfaces, it is hoped that they will also provide a theoretical framework for the interpretation of such optical measurements.

For high-area electrocatalysts, photoacoustic spectroscopy may be more useful for obtaining UV-visible spectroscopic data.

In an attempt to obtain vibrational information for adsorbed species, several electrochemists have turned to infrared attenuated total reflection spectroscopy and recently to Raman spectroscopy. The infrared studies are restricted by the requirement of infrared-transparent substrates (e.g., Ge, Si) and solvent interference. Ordinary Raman techniques lack sufficient sensitivity for monolayer levels on low-area electrodes but resonant Raman overcomes this problem. Simple organics adsorbed on smooth electrode surfaces have been successfully examined by the resonant Raman technique and have yielded good signal to noise.

Photoelectrochemical effects have proven to be a powerful tool for the study of semiconductor electrodes and have been extensively used for this purpose since the 1950's. Photo-assisted electron transfer has also been studied at metal electrodes but so far has not yielded much surface information.

In a few instances, Mössbauer spectroscopy has been applied successfully to electrode surface studies, particularly to the formation of underpotential-deposited monolayers of Sn on Pt and passivation layers on iron.

Electron spin resonance has been used to examine solution-phase intermediates produced in electrochemical reactions. This method should also be applicable to adsorbed radical species on dispersed electrode particles such as carbon.

The potential can be controlled in various ways, e.g., the Gerischer dispersed-electrode technique or the introduction of various redox couples.

In light of the important developments in solid state NMR, the question arises as to what extent NMR may be able to provide information concerning passivation layers, high-area oxide electrodes of the type used in batteries and adsorbed species on high-area electrodes. The development of techniques in this area should be encouraged.

2. Non-In Situ Techniques

Unfortunately the elegant surface-electron physics techniques cannot be applied in situ. Even so, they are proving a powerful tool in electrochemical surface studies in several ways.

a. Elemental compositional changes and impurity effects

Many electrochemists examine their electrode surfaces before and after electrochemical studies using ESCA and Auger to check on elemental compositional changes and particular poisoning effects. Such techniques have been directed, especially to passivation layers on both active and noble metals.

b. Valency state of electrocatalysts and oxide layers on metal

Several electrochemists have attempted to use ESCA (chemical shifts) to establish the valency state of oxide layers and other electrocatalyst layers on metal substrates. Even with controlled atmosphere transfer between the electrochemical and high-vacuum environments, the probability of valency

state changes following removal of potential control is quite great in most instances and hence great care must be exercised in interpreting such studies.

c. Single crystal-clean surface experiments

The orderly development of electrocatalysis as a surface science requires single-crystal studies to establish the relation of the electrocatalysis to surface crystal structure. In such studies, LEED-coupled Auger provides a means to establish that a clean surface of a predominantly one-surface structure has been prepared. The problem is to transfer the specimen from the ultrahigh vacuum of the LEED-Augur system into the electrochemical environment without restructuring and contamination occurring during the transfer or while within the electrochemical cell. Several laboratories have developed special transfer techniques to minimize such changes and have achieved some degree of success in the study of hydrogen adsorption on single-crystal platinum. These studies indicate a large dependence of hydrogen adsorption and the double layer properties on various crystallographic surfaces.

The return of the single-crystal electrodes to the LEED-Augur system has also been attempted, but the loss of potential control and the complete volatilization of the electrolyte present some problems. Vacuum sublimation of a completely volatile electrolyte (e.g., dilute aqueous HF or NH_4OH) at low temperature appears promising.

d. Parallel solid-gas and electrochemical experiments

In some instances parallel adsorption studies can be performed on a particular surface in the gas or vacuum environment and the electrochemical environment. Such experiments are helpful in gaining insight into the sites and chemical properties of adsorbed species. Care must be taken not to over-interpret such comparisons since the two types of interfaces have pronounced intrinsic differences.

3. Instrumentation

Access to the following instrumentation is desirable for the development of electrochemical surface science in addition to the usual electrochemical instrumentation present in well-equipped electrochemical laboratories (see Table 4).

In addition, NMR equipment may become useful for examining the structure of various electrocatalytic species and battery oxides adsorbed species on high-area electrodes as advances are made in the solid state NMR.

Question II-1: Select several highest priority research areas which should be supported in the near future: rank these if possible.

Answer: High-priority research areas:

1. Near term: to have significant impact on technology within 5 to 10 years.
- a. Electrocatalysis

(1) Hydrogen electrocatalysis (anodes and cathodes)

Studies of mechanisms, rate constants, and transfer coefficients on various electrode surfaces for which data are not available

in the literature; hydrogen electrosorption studies using electrochemical methods; relation of these quantities to electronic structure of catalyst, and to electrolyte composition; impurity effects (including CO, H₂S, NH₃); choice of surfaces for study to be guided by expected heats of H adsorption and volcano curve considerations; special emphasis on non-noble metal catalysts and acid electrolytes.

(2) Oxygen electrocatalysis (cathodes and anodes)

Parallel studies to those for hydrogen electrocatalysis; catalysts to be examined to include defect-transition metal oxides, adsorbed transition metal ions, and stable complexes on carbon and graphite substrates; doped carbons and graphites, derivatized carbons and electronic conducting oxides; special emphasis on non-noble metal catalysts in acid and alkaline electrolytes.

Useful research background: electrochemistry, metallurgy-ceramics, inorganic chemistry, solid state and surface physics.

b. Morphological changes in high-area electrocatalyst systems

Research to establish mechanism of sintering and restructuring of high-area electrocatalysts, particularly noble metals on carbons and graphites.

Useful research background: electrochemistry, metallurgy, surface physics.

Table 4. Instrumentation of electrochemical surface science research.

Instrumentation	Types of Electrochemical Research
I. In situ studies	
A. Optical instrumentation	
1. UV-visible reflectance	Electrosorption, reaction intermediates
2. Automatic ellipsometer for UV-visible tuned laser	Passivation, electro-adsorption
3. Raman instrumentation including UV-visible tuned laser	Electrosorption, reaction intermediates
4. High intensity UV-visible-infrared tuned laser	Band gap, surface state studies of semiconductor electrodes, photo-assisted charge transfer processes
B. Mössbauer spectrometry	Passivation in iron; certain electrocatalysts
II. Non-in situ	
A. Surface physics	
1. ESCA	surface composition of electrode surfaces
2. Auger	surface composition
3. SAM	distribution of surface components
4. LEED	single-crystal studies
5. SIMS	surface composition, including H and molecular fragments
B. Electron microscopy diffraction	catalyst particle size and structure; electro-crystallization

Table 4. Continued.

C. X-ray diffraction	bulk structure, catalyst particle size
D. BET surface area	surface areas and pore distribution in high area electrodes
E. Differential thermoanalysis	properties of oxides, particularly battery oxides
F. ESR	to check on radical reaction intermediates and possibly adsorbed radicals in high- area semiconductor electrode surfaces

c. Dendrite and other morphological changes with metal electrodes (e.g., Zn in aqueous electrolytes, lithium in molten halides)

Studies of electrocrystallization and electrodisolution as functions of potential, electrolyte, poisons, and temperature; studies of electronucleation, adatom and adion mobilities. Useful research background: electrochemistry, metallurgy, surface physics.

d. Wettability of electrode surfaces: surface energies and contact angles

Determination of the factors controlling interfacial energies and contact angles through measurements with various electrode materials in aqueous electrolytes and molten salts; effects of adsorption, chemical interactions.

Useful research background: electrochemistry, surface physical chemistry.

2. Longer range surface science research: to have significant impact on technology in next 10 to 20 years.

a. Electrocatalysis

(1) Theoretical studies. Calculation of heats of adsorption, potential energy surfaces for charge and atom transfer, and rates for component steps.

Useful research background: theoretical chemistry (interacting with electrochemists and surface physicists).

(2) Experimental studies on single crystal surfaces.

Electrochemical measurements of adsorption isotherms, heats of adsorption and rates for hydrogen and oxygen electrode reactions on noble metal single-crystal surfaces including high-index surfaces; LEED, Auger-ESCA characterization of surfaces with special transfer techniques; comparison of electrochemical measurements with counterpart measurements at gas-solid interfaces.

Useful research background: electrochemistry and surface physics (interacting with theoretical chemists).

(3) Systematic studies of hydrogen and oxygen electrocatalysis on various electrocatalysts of both high and low activity to establish electronic and structural factors; studies to include, e.g., derivatized surfaces, intercalation compounds, mixed transition metal oxides (valency stabilization through additions of various doping agents), and various highly adsorbed transition metal ions, complexes, and underpotential electro-deposited species.

Useful research background: electrochemistry, metallurgy-ceramics, inorganic chemistry.

b. Development of new in situ techniques for obtaining molecular level information concerning electrochemical interfaces.

(1) Theoretical interpretations of optical properties

of electrochemical interfaces, particularly with the adsorption of various species.

(2) Development and optimization of in situ techniques for studying adsorbed species; e.g., resonant Raman, NMR, ESR, photoacoustic spectroscopy.

Useful research background: electrochemistry, chemical instrumentation, electronic and vibrational spectroscopy, NMR and ESR spectroscopy.

Question II-2: How would you organize the surface science research so that it has maximum impact on the various energy technologies? How would you optimize the research development technology information flow?

Answer: To expedite such flow it is recommended that annual workshops be established to bring together about 25 people in particular areas with representation from the relevant scientific disciplines and the potential users. Such workshops should be integrated into the grant-reporting structure so that grantees as well as government researchers are expected to attend and report on their research results.

1. Critical mass of research groups in electrochemical surface science in the U. S. A.

a. Theoretical area: Critical mass does not exist.

(Only two or three U. S. scientists have contributed much to the theoretical aspects of electrocatalysis.)

b. Experimental area:

(1) Fundamental science: at the best marginal and probably below critical mass, particularly with respect to electrochemists who have strong surface chemistry-physics backgrounds. This area warrants at least six to eight academic groups focusing on electrocatalysis; the present number is much less--three or four. (Substantial fundamental electrocatalysis research is being carried out in a few government laboratories, particularly Brookhaven and Fort Belvoir.)

(2) Applied research: probably has critical mass, principally in industrial laboratories. (Proprietary interests however, interfere with free communication.)

2. Major obstacles to close cooperation between national laboratories and industry

The principal obstacle is the proprietary interests of industry.

One way to promote cooperation between national laboratories and industry is for the national laboratory to have access to the proprietary information on the condition that it be treated as classified. Such an arrangement does not, however, help information flow with the academic community.

Question I-5: Are there important areas of surface science research that impact on energy technology where the best work is carried on outside the United States? Please indicate where.

Answer: The principle international center for basic research in electrochemistry including electrocatalysis is the Institute of Electrochemistry of the Soviet Academy of Sciences in Moscow, with approximately 450 scientists. In addition, the Karpov Institute of Physical Chemistry and the Soviet Academy's Institute of Physical Chemistry have several hundred electrochemists engaged in more or less basic research in electrochemistry with a heavy emphasis on passivation phenomena and corrosion.

Other world centers of fundamental research in electrochemistry surface science which surpass in size any single group in the U. S. include:

- 1) the electrochemistry group in the Institutes of General and Inorganic Chemistry in Kiev (Ukrainian Academy of Sciences);
- 2) the Fritz-Haber Institute of the Max Planck Society in West Berlin;
- 3) the CNRS and University research groups in Paris and Bellevue, France;
- 4) the electrochemistry group at the University of Southampton under Professors M. Fleischmann and G. T. Hills.

In addition to the USSR, England, France, and Germany, there is substantial research in electrochemical surface science in Japan, Czechoslovakia (Institute of General Chemistry, Prague), Yugoslavia (Belgrade, Skopje, Zagreb), Italy (Milan), Bulgaria (Sofia), and Canada (Ottawa).

Question II-6: (a) How would you provide a mechanism to educate technical personnel for employment in the various energy technologies?
(b) How would you provide a mechanism to retrain technical personnel already working in the energy technology fields, in modern surface science?

Answer: Education and retraining of technical personnel in modern surface science:

1. Sabbatical Leaves

The academic community benefits greatly from sabbatical leaves which help a faculty member to catch up with studies in his own field and to enter new research areas. The same approach is recommended for industrial and government scientists. They should be allowed sabbatical leaves taken in academic or other laboratories where they have an opportunity to study and gain experience in modern surface science and the relevant techniques.

2. Workshops

One means for making technologists aware of contemporary developments in surface science is to hold small workshops where surface scientists have an opportunity to summarize new developments and for the technologists to communicate about their particular problems. This is a good way to close the feedback loop between fundamental research and technological development work. Such workshops need to have small attendance (~25) with much time for informal discussion.

● PASSIVATION OF SURFACES

D. Corrosion

R. Staehle, Chairman Ohio State University	J. Morris, Jr. Lawrence Berkeley Laboratory
J. Apps Lawrence Berkeley Laboratory	P. Palmberg Phys. Electronics Industries
J. Blakely Cornell University	J. Rowley Los Alamos Sci. Lab.
H. Frederikse National Bureau of Standards	S. Wolf ERDA
D. Michels Idaho National Engr. Lab.	

With respect to the subject of corrosion the group considered that the field of surface science is too narrowly confined. Work in surface science should contribute also to understanding corrosion phenomena such as stress corrosion, cracking, hydrogen embrittlement, corrosion fatigue, and erosive wear. These and other phenomena concern liquid-solid interfaces which, as a class, are under-studied in comparison to their importance to technology and society.

Question I-3: Identify, if possible, the long-range surface science research problems where much effort should be concentrated.

Answer: Table 5 suggests the variety of environments in which surface science might play a role in helping to produce energy for industrial and domestic uses. Effort could be concentrated on:

- 1) Formation of a new phase on a clean surface (e.g., oxide or carbide on steel, SiO_2 on SiC), consisting of
 - a) nucleation of the new phase;
 - b) growth of the new phase;
 - c) structural aspects of the new phase;

Table 5. Surface science problems related to corrosion in the various energy technologies.

Class	Environment			Solvents	Solutes	Processes Involving Surface Problems
	Pressure (atm)		Temp. (°C)			
	Gas	Liquid				
Solar						
Direct	~1	~1	0 to 80	Glycol, H ₂ O	Additives, phosphates, alums	UV degrad. metal, glass corrosion, corrosion in heat storage units, particulate adhesion to transparent surfaces
Ocean, thermal, mechanical	~1	1 to 300	0 to 25	H ₂ O	Biota, seawater	Biofouling, seawater corrosion
Fossil						
Coal						
Conventional	0.05 to 30	1 to 30	0 to 700	H ₂ O, flue gases	Additives	Corrosion, ionic scales
Gasification	1 to 120	1 to 5	0 to 2000	Org. mix, slags		H ₂ S, H ₂ -alloy effects, organic scale buildup
Oil shale	0.1 to 5	~1	0 to 600	Slags	Solids	High temp. corrosion/erosion
Tar sands	0.1 to 5	~1	0 to 200	Org. mix	Solids	H ₂ -alloy effects, organic scale buildup
Oil, conventional, enhanced recovery	1 to 300	1 to 300	1 to 200	H ₂ O, petroleum	Ionic salts	H ₂ S effects, ionic salts, corrosion, scaling
Biomass						
Fermentation	~1	~1	20 to 40	H ₂ O, org. mix	Org., inorg. CO ₂	Atm. corrosion
Pyrolysis	1 to 100	1 to 100	0 to 600	Org.-inorg. mix		CO ₂ , corrosion by N- and S-containing molecules
Geothermal						
Electrical	0.05 to 20	~1	80 to 300	H ₂ O, org.	Ionic salts	Erosion/corrosion, H ₂ S, ionic scaling
Processing & heating	1 to 3	1 to 3	20 to 300	H ₂ O, glycol	Ionic salts	Ion-stimulated corrosion, inorganic scaling
Reinjection	~	1 to 150	0 to 50	H ₂ O	Ionic salts, org. additives	Rock-fluid interactions, scaling
Nuclear						
Fusion	10 ⁻⁶ to 1	~1	High T			
Fission	1 to 20	1 to 20	0 to 700 and high T	H ₂ O, liq. metal		
Environmental control	~1	~1	-20 to 50	H ₂ O, atm.	Ionic salts, trace elements	Water treatment (F- removals, etc.) Gas scrubbing (H ₂ S, Rn, etc.)

- d) thermodynamics and kinetics of the new phase;
 - e) theory for chemical bonding of a new layer to a substrate, distinguishing between growth on self and non-self substrates.
- 2) Adhesion of the new layer (experimental techniques, scaling, spalling--for liquids wettability).

Corrosion begins with nucleation and growth of a monolayer.

However, it is important to study layer growth to thicknesses of several hundred Angstroms or even microns.

- 3) (Clean) surface characterization (solids in vacuum), including
- a) electronic states;
 - b) defect structure, defect distribution, and selectivity (the analogy with catalysis deserves note);
 - c) near-surface regime--the structural and compositional contrasts with the interior parts (which have a classical description).
- 4) Solid-liquid interface, including
- a) morphology and electronic structure of the solid near the liquid;
 - b) morphology and electronic structure of the liquid near the solid;
 - c) development of experimental approaches for studying the solid-liquid interface, e.g., optical, electro-chemical and other methods;
 - d) study of the barrier layer in the liquid-solid interface (electronic states, electric fields, compositional discontinuities, etc.).

- 5) Arcing (surface in very large electric fields),
consisting of
 - a) effects on surface structure;
 - b) evaporation and (re) condensation;
 - c) charge transfer.
- 6) Surface modification/protection, including
 - a) development of theory and experiment relating to activation of surface sites for subsequent acceptance of inhibitors (with an emphasis on organic inhibitors) or macroscopic coatings;
 - b) research into improved surface coating methods studying
 - i) gas or liquid transport,
 - ii) atom (or molecule) dynamics as it approaches the surface,
 - iii) atom (or molecule) diffusion after impinging upon the surface, e.g., surface diffusion,
 - iv) film stresses.
- 7) Corrosion of materials, e.g., metals, ceramics, polymers, composites. Theory and experiment relating to
 - a) oxidation,
 - b) sulfidation, and
 - c) carburization or other gas effects.

Note: Emphasis on metals and glass is through "chemisorption" or monolayer growth, whereas the emphasis on ceramics and glasses is their defect structure and physical properties once a discrete product layer has been formed.

8) Interaction between environment and mechanical properties, consisting of

- a) theory and experiment investigating adsorption and chemisorption with respect to surface energies, crack growth and defect configuration at the intersection with the "contaminated" surface.
- b) relation of above to "engineering" properties, e.g., stress corrosion, cracking, corrosion fatigue, hydrogen embrittlement, slow crack growth, etc.

Question I-4: Which are those areas of surface science that are neglected although research in these areas would be important in support of one or several of the energy technologies?

Answer: Surface "science" studies are presently heavily concentrated on metals and semiconductors and involve low pressure ($\leq 10^{-4}$ Torr) and low temperature ($\sim 300^\circ\text{K}$) conditions. Current techniques of surface science should be applied to a wider range of materials and experimental conditions. Specific recommendations regarding areas of research currently neglected or with low levels of activity are as follows:

- 1) Some theoretical effort should be devoted to the topic of surface structure (electronic, vibrational, defect, etc.) at elevated temperature. Experiments on the detection of surface defects and their effect on binding and transport properties are required.

- 2) Further work deserves to be done on the structure and reactions at the interface between metals and relatively high pressure (~ 1 atm) gases using techniques such as LEED, electron, ion and optical spectroscopies, ellipsometry, etc.

- 3) Surface characterization of nonmetallic materials is required. This should include covalent and ionic crystals

and oxide semiconductors, as well as some more complex systems such as slags, molten salts, and polymeric materials.

4) The defect structure of scales (oxide and oxyanion salt films) is of importance in connection with growth and passivation characteristics. Further data on the electrical and thermal conductivity of scales would be valuable.

5) The structure of solid-solid interfaces requires further study for the development of strongly adherent protective coatings on metals. High spatial resolution techniques would be valuable.

Question I-5: What sort of physical-chemical data are missing in the field of surface science that would help develop new technologies or better control existing technologies?

Answer: Several types of physical-chemical data are needed to help in developing passivation coatings and in understanding corrosion phenomena. They include:

- 1) thermodynamic properties of concentrated electrolytes;
- 2) thermodynamic properties of compounds;
- 3) phase diagrams for two dimensional systems, for example, pressure, temperature, thickness diagrams for the oxidation of metals;
- 4) atom or molecular diffusion coefficients on metal surfaces;
- 5) atomic structure of various substrate-adsorbate systems;
- 6) parameters which govern the growth rate of surface films.

Question I-6: What classes of surfaces need to be better understood at the basic level in order to assure better control of surface processes? What sort of material or process characterization is needed to help develop new technologies or better control existing technologies?

Answer: Classes of surfaces that need scientific attention are dealt with in Table 6 and in the following discussion.

The industrial use of energy involves its conversion from one form to another or into a different medium. In both cases a physical interface is involved. Important heat transfer events involving atomic and molecular activity occur at the phase boundaries.

The nature of the phase boundary in the context of heat transfer is an interfacial region, a tubular zone having a finite thickness often much greater than a monolayer. This interfacial region provides a transitional space for the homogeneous phases on either side. Since the two sides frequently have different temperatures and different compositions, some irreversible chemical phenomena take place.

Study of this kind of interface involves a logical extension of surface science. In principle, a classical surface would be studied by beginning from a clean condition, proceeding through nucleation events for the development of a new phase on the substrate, and continuing with the lateral extension of the new phase and its extension into the "free" space of the "z" direction, reaching thicknesses of many atomic layers.

Table 6. Classes of surfaces that need scientific attention.

	Environment				Processes Involving Surface Problems
	Pressure (atm)				
	Gas	Liquid	Temp.	Solvents	
Conservation					
Heat Transfer					
Insulation					
Useful	~1 to 30	~1 to 20	20° to 1500°C	Aqueous, homogeneous	Scale deposition and corrosion at the following interfaces: 1) metal-aqueous solution 2) metal-high T&P gas 3) ionic solid-aqueous solution
Hydride	~1	~1	20° to 200°C	Metal	Container corrosion, contamination
Fuel cell	~1	1 to 15	20° to 1000°C	Acid, molten salt	Container corrosion, contamination
Batteries	~1	1 to 10	20° to 500°C	Li, S, H ₂ SO ₄	Container corrosion
Superconductors	~1		0°K to 50°C	He, H ₂	Container oxidation of conductor and fittings during shutdown

The medium in the free space can usefully be a gas, perhaps dilute at first. However, more useful information will come from the study of the effect of more dense gases and ultimately condensed fluids. Such endeavors mark a transition from surface science, as traditionally practiced, to a science of interfaces.

In addition to the concept of an interface as a subject for study, the dynamic nature of industrial processes deserves scientific attention. The process is, microscopically, a series of molecular events which can be evaluated by study of the thermodynamics, statistical mechanics, chemical bonding, and other science concepts, taken in real time. Such an approach would be a science of interfacial processes.

Although a large variety of interfaces are possible, the ones of greatest importance to energy development are few in number. Significant among these are aqueous-metal interfaces in which corrosion and scaling occur due to the dissolved components. In some cases heat transfer is important, especially with respect to gas-metal interfaces in reaction vessels. Aqueous-oxide and gas-oxide interfaces are important in the context of ceramics or when the metal substrate presents an oxide surface to the contacted fluid.

Very little scientific information about the interfacial region is available. Structural information would be valuable. Surface bonding modes for molecules and ions are expected to be different from gas-solid counterparts, since solvation

competes for the molecular association on one hand and the solvent and extraneous ions compete for surface sites on the other hand. The consequences of these near-surface phenomena control the usefulness of the equipment. In principle they can be described in terms of such concepts as electron sharing, statistical mechanics, etc. If scientific data were available concerning chemical bonding and the principles of intermolecular competition, better estimates could be made of the engineering parameters required for design of novel systems or the incorporation of novel material combinations into practical designs.

Question I-7: What theoretical research technique offers the most promise for actual predictive power?

Answer: Of chief importance to a description of an interface are the geometrical facts, and the composition and distribution of components. Resolution in space involves three dimensions, of which the z direction can be of the order of microns in thickness. Lateral resolution should provide information about growth rates of developing films and, in some experiments, the character of nucleation sites for growth of scale or corrosion products, or the initiation of etch pits or corrosion attack.

A few techniques apply--namely ellipsometry, high voltage electron microscopy (HVEM; particularly with environmental chambers, energy loss analysis or both), and laser Raman spectroscopy. The first technique yields information on film thickness and spread of growing films in situ. HVEM

can give in situ data at high resolution, perhaps identifying nucleation sites or processes occurring at a spreading edge. Raman techniques yield information about molecular species or bond types; of particular significance are newly developed techniques using crossed laser beams which stimulate a small volume of fluid and can be ranged through the interface, including the z direction.

Because these techniques are new, the real opportunities for studying thick interfaces are just becoming available. These tools promise information about the interfacial region that includes real-time analysis with good spatial resolution.

Question I-8: Describe the experimental techniques and the type of instrumentation needed to obtain the necessary surface science data or surface characterization.

Answer: Because of the complexities associated with corrosion phenomena, a range of instrumental techniques, falling into six categories, are required for the study of surfaces and surface-related phenomena. They are listed below.

1) Electron microscopy:

- a) high resolution EM (this technique might cause radiation damage to the surface),
- b) raster emissions,
- c) energy loss spectroscopy,
- d) application of environmental chambers,
- e) scanning electron microscopy.

2) Field ion microscopy

3) Optical methods:

- a) Raman-laser spectroscopy (particularly with respect to molecular surfaces),
- b) optical microscopy (reflection, ellipsometry),
- c) high-intensity light.

4) High-vacuum electron and ion emission techniques for surface analysis:

- a) Auger electron spectroscopy,
- b) scanning Auger spectroscopy,
- c) ion scattering spectroscopy (ISS),
- d) secondary ion mass spectrometry (SIMS),
- e) electron spectroscopy for chemical analysis (ESCA),
- f) exoelectron emission.

5) Miscellaneous spectroscopic techniques:

- a) Newton spectroscopy,
- b) Mössbauer spectroscopy.

6) Electrochemical techniques:

- a) electrochemical potential distribution,
- b) general electrochemical methods.

Question II-1: Select several highest priority research areas which should be supported in the near future: rank these if possible.

Answer: The group agreed that the highest priority for research in surface science pertinent to corrosion involves three considerations: a model system, specific environments and specific substrates.

The model system is a solid surface in a molecular environment which may be either gas or liquid. This model system should

be considered at three stages: adsorption at specific sites, lateral spreading of the first layer, and growth of multiple layers. The interaction of the substrate should be considered since its structure may change in the process of interaction, e.g., the substrate may become ordered.

Specific substrates should be considered for the following:

- 1) metallic substrates should emphasize iron and iron base alloys;
- 2) metallic materials used as containers for high-temperature processes, e.g., Al_2O_3 and ceramic materials used for turbine blades, e.g., SiN-SiC;
- 3) glasses as used for container materials;
- 4) polymeric solids used as structural materials.

Gaseous and aqueous environments should be studied where dissolved species are mainly hydrogen, sulfur, and oxygen with a secondary emphasis on chlorine, nitrogen, and carbon.

As seen from the perspective of corrosion problems in energy technologies the consensus is that questions II-2, II-3, II-4, and II-6 relate largely to the management and interactions of people. The basic mechanisms for these interactions are rather well known and are perhaps best represented by organizations of interdisciplinary seminars, workshops, and overview articles on both technological problems and research results.

Surface science research efforts directly related to corrosion problems largely do not exist currently. Efforts to encourage

institutions and research groups to work on corrosion problems and the development of equipment to perform multievaluations/measurements on reacting surface interfaces would appear to be valuable directions to pursue. A call from users/technologists for "handbook" type data compilations for the research community might provide valuable resource documentation as well as promote professional interactions.

The reduction of obstacles between the national laboratories and industrial firms depends upon development of appropriate incentives on both sides.

A major issue in research and development technology information flow is need for stronger interactions between and within the various ERDA divisions.

Question II-5: Are there important areas of surface science research that impact on energy technology where the best work is carried on outside the United States? Please indicate where.

Answer: Areas of surface work being carried on outside the U. S.

relevant to corrosion are the following:

- 1) energy loss spectroscopy in Germany;
- 2) high-voltage and high-resolution electron microscopy in Germany, England, and Japan;
- 3) electrochemical kinetic studies of film-free alloys in the USSR;
- 4) organic inhibitors in the USSR;
- 5) molten salt electrochemistry in the USSR and Germany.

E. Interaction of Ions with Surface and Near-Surface Regions

J. Mayer, Chairman	D. Gruen
Calif. Inst. of Tech.	Argonne National Laboratory
W. Bauer	F. Vook
Sandia Laboratories	Sandia Laboratories
C. Colmenares	G. Wehner
Lawrence Berkeley Laboratory	Arizona State University

Question I-1: The various fields of ERDA's mission include energy conservation, fossil, nuclear fusion, geothermal and solar energy technologies and environmental control. Identify the fields where most of the surface science problems are concentrated.

Answer: The energy technologies of fission, fusion, fossil, solar, and geothermal have surface, near-surface, and interface problems which are crucial to their success. For example, magnetic fusion progress is now limited by a need to solve the plasma contamination by first wall surfaces. The interaction of energetic ions with surfaces is a highly successful research area which is providing basic insight and data for applied energy problems. The two major areas of application of ion beams to surfaces are ion-surface modification and ion-surface analysis. Included in ion surface modification is ion implantation, both to beneficially modify the near surface (corrosion protection, solar cell junctions, erosion, and wear) and to provide tailored surface environments for particular applications. The study of basic phenomena such as sputtering, diffusion, solubility, phase diagrams, corrosion, oxidation, and radiation damage simulation plays an important role in this work.

The following table enumerates the various energy technology problems that may be investigated by ion-surface modification.

Question I-3: Identify, if possible, the long-range surface science research problems where much effort should be concentrated.

Answer: Long-range science research problems are:

- a) chemical and physical sputtering, including back reflection and gas re-emission;
- b) near-surface modification of composition, microstructure, and topography;
- c) adsorption and desorption phenomena;
- d) chemisorption;
- e) influence of impurities on sputtering phenomena, surface migration, near-surface diffusion and solubility.

Question I-4: Which are those areas of surface science that are neglected although research in these areas would be important in support of one or several of the energy technologies?

Answer: Neglected but important surface science research areas are: systematic application of ion beams to surface analysis and surface modification with specific technological interactions, e.g., corrosion, erosion, embrittlement, catalysis (Table 7).

Question I-5: What sort of physical-chemical data are missing in the field of surface science that would help develop new technologies or better control existing technologies?

Answer: Needed physical-chemical surface data are:

- a) low-energy sputtering data (i.e., sputtering yield of engineering materials);

Table 7. The role of ion beams in energy technology.

Energy Field	<u>Surface Modification</u>	<u>Surface Analysis</u>
	Implantation of Ions	SIMS, RBS, Nuclear Reactions, ISS, Sputter Auger and ESCA
Fusion	First wall-plasma simulation (sputtering, desorption). New superconducting films. Coatings for laser fusion and beam fusion. Pellet technology. Ion polishing of mirrors. Corrosion of cooling ducts.	Confinement experiment analysis. First wall analysis.
Fission	Neutron damage simulation. Waste disposal studies. Corrosion by liquid metal coolants. Isotope separation via sputtering.	Cladding vessel analysis. Fracture analysis.
Fossil	Hydrogen diffusion barriers, to avoid embrittlement. Catalyst modification. Modification for erosion and wear surfaces. Corrosion of vessels.	Catalysts analysis. Hydrogen containment vessel analysis. Fracture analysis.
Solar	Sputter deposition for mirrors, photovoltaic junction contacts, and passivating layer formation. Production of thermal absorbing layers.	Mirror and composite layer analysis. Solar thermal absorbing coatings.
Geothermal	Drill surface modification. Erosion and high wear surfaces. Nonsticking corrosion-free surfaces.	Analysis of interface between deposits and metals. Adhesion analysis of strippable layers.
Environmental		Automotive catalyst degradation analysis. Pollution analysis of solid, liquid, and gas samples.
Conservation	Corrosion in thermal storage media (molten salts, organics).	Surface analysis of storage media such as metal hydrides.

- b) data elucidating the sputtering process in compound materials and data on sputtering thresholds;
- c) formation of compounds with high-dose ion beams;
- d) formation of near-surface diffusion barriers;
- e) data on diffusion, segregation, and embrittlement.

Question I-6: What classes of surface need to be better understood at the basic level in order to assume better control of surface processes? What sort of material or process characterization is needed to help develop new technologies or better control existing technologies?

Answer: Classes of surfaces that need to be better understood are: supported metal catalysts, engineering surfaces (e.g., fusion, first walls, corrosion processes), and semiconductor interfaces and junctions.

There is also a need to develop new technologies and control existing technologies, and to develop higher resolution surface barrier detectors and longer lasting electron detectors.

The ion surface analysis tools listed in the table are particularly useful for process characterization, but need to be refined and improved to meet future needs.

Question I-7: What theoretical research technique offers the most promise for actual predictive power?

Answer: Theoretical surface science research needs:

- a) Monte Carlo theory (ion beam interaction with surfaces);
- b) statistical chemical theory;
- c) improvement of data base on which to base theory;
- d) sputtering theory, including impurities and surface morphology.

Question I-8: Describe the experimental techniques and the type of instrumentation needed to obtain the necessary surface science data or surface characterization.

Answer: The instrumentation and experimental techniques needed for surface characterization are:

- a) ion beam technology coupled to electron spectroscopies;
- b) techniques to examine the surface/liquid interface.

Question II-1: Select several highest priority research areas which should be supported in the near future: rank these if possible.

Answer: We believe that ion beam analysis, simulation of radiation damage, and modification of materials can have a major impact in the energy field. The rank order of the highest priority research areas is:

- a) low-energy ion interactions with surfaces, including charge states, charge exchange excitation, photon emission, and sputtering yields;
- b) surface and near-surface modification using ion beams (composition, topology, microstructure) including diffusion and solubility measurements (surface, near-surface, and grain boundary), measurement of equilibrium or steady state phase diagrams, and production of new materials and metastable phases, and solubility and segregation under high flux and fluence conditions;
- c) corrosion, oxidation, and passivation by use of ion beams.

Question II-2: How would you organize the surface science research so that it has maximum impact on the various energy basic materials and process control information in technologies? How would you optimize the research development technology information flow?

Answer: Our recommendations cover two areas:

1) Information transfer on the working level. We propose the creation of a fund for travel and experimental equipment which will enable applied scientists to work at laboratories and universities struggling with basic problems. Also provide consulting funds for basic scientists to work at applied labs.

2) Establishment of joint science-technology surface conferences (e.g., on corrosion and catalysis) as now exist for ion implantation in semiconductors and fusion areas.

Question II-3: What do you consider as the critical mass of research groups in surface science to provide the necessary basic materials and process control information in your area of concern? Do we have this critical mass?

Answer: Surface analysis experimentation is capital intensive especially when coupled with ion beams. At present only a few labs have critical mass capacity. Therefore interaction between labs is necessary for rapid and efficient progress.

Question II-4: What are the major obstacles in the way of developing close cooperation between national laboratories and industry? How could these obstacles be best removed?

Answer: There is no motivation to interact because of industrial proprietary restrictions. Also, basic researchers in universities have difficulty finding the real problems that should guide their research. Perhaps some of these obstacles could be removed by organizing joint science-technology conferences

in special surface science areas. Basic groups must be encouraged to support basic labs and universities.

Question II-5: Are there important areas of surface science research that impact on energy technology where the best work is carried on outside the United States? Please indicate where.

Answer: In the field of particle-solid interactions the following list gives areas of foreign superiority:

Great Britain--surface modification for corrosion research;

Germany--ion scattering and surface analysis for first wall problems;

Denmark--atomic collisions theory;

USSR--ion scattering and sputtering;

Japan--ion implantation for large-scale semiconductor manufacture.

Question II-6: (a) How would you provide a mechanism to educate technical personnel for employment in the various energy technologies?
(b) How would you provide a mechanism to retrain technical personnel already working in the energy technology fields, in modern surface science?

Answer: We propose to retrain technical personnel working in various energy technologies through exchange programs with laboratories and universities. We note that the Europeans and Japanese are using this method to educate and retrain their people much more than is the U.S.

F. Grain, Phase Boundaries and Interfacial Boundaries
(Adhesion, Lubrication)

C. McMahon, Chairman	J. Houston
University of Pennsylvania	Sandia Laboratories
M. Brodsky	J. Jenkins
Argonne National Laboratory	Oak Ridge National Laboratory
J. Burton	D. Maddox
Exxon Res. & Engr. Co.	Sandia Laboratories
	D. Stein
	Michigan Tech. Univ.

A primary concern in the field of energy technology is the stability of materials under service conditions. Failure of materials commonly involves loss of cohesion or adhesion at interfaces as a consequence of embrittlement or corrosive processes. Such phenomena can involve either internal reactions which alter interfacial structure and/or composition or reactions with the external environment. In order to predict and control these phenomena, a basic understanding of interfacial structure, composition, and reactions is required. To this end, it is essential to employ the concepts and techniques of surface science.

I. Important problem areas in energy technology include:

- 1) embrittlement of crystalline materials, such as steel, Ni-based alloy, refractory metals, noble metals, and ceramic materials;
- 2) effects of aggressive environments (e.g., H_2 , H_2S , liquid metals, aqueous solutions) on materials;
- 3) adhesion of joints and coatings;
- 4) control of microstructure by surface-related phenomena (e.g., texture formation in Si steels for transformer applications).

II. The underlying scientific problem areas include:

- 1) the understanding of the structure of interfaces, consisting of
 - a) crystallography,
 - b) composition,
 - c) defect structure,
 - d) phase relationships,
 - e) dynamic behavior, i.e.,
 - i) diffusion in various potential gradients, and
 - ii) internal and environmental chemical reactions;
- 2) how to measure interface strength to determine fundamental quantities amenable to theoretical analysis--normal strength and shear strength of grain boundaries and other interfaces, i.e., bonded joints, coatings, etc.;
- 3) factors which control strength of interfaces, namely,
 - a) structure (atomic arrangements),
 - b) composition (atomic species);
- 4) factors which control solute segregation to interfaces, namely,
 - a) thermodynamic,
 - b) kinetic,
 - c) atomic structure of interfaces;
- 5) how grain boundaries interact with various environments, including studies of
 - a) surface dissolution;
 - b) boundary decohesion, initiated,

- i) at the surface, and
- ii) internally.

III. Areas of surface science which need to be extended or developed
(in order of priority):

- 1) experimental and theoretical studies of correlations between free surfaces and grain boundaries with respect to
 - a) segregation,
 - b) diffusion,
 - c) structure, and
 - d) phase equilibrium (2-dimensional);
- 2) determination of grain boundary and interface structure (atomic arrangements, defect structure) which necessitates
 - a) development of diffraction techniques to probe grain boundary structure (i.e., LEED, RHEED),
 - b) examination of other non-diffraction techniques for this purpose (e.g., FIM),
 - c) improvement of spatial and depth resolution of electron spectroscopy,
 - d) development of the technique of combined high resolution electron microscopy (e.g., lattice imaging) and electron spectroscopies (Auger, energy loss, etc.);
- 3) determination of grain boundary composition (atomic species, bonding, i.e., what atoms are present and how are they associated?), in particular the development of quantitative

- a) calibration of AES for quantitative chemical analysis,
 - b) theory of Auger emission, consisting of studies in
 - i) effects of atomic environment,
 - ii) line shape analysis, and
 - iii) angular resolved AES;
 - c) theory and technique of depth profiling of chemical composition;
- 4) development of
- a) surface techniques for measuring thermodynamic activities in solid solutions (e.g., effects of solute interactions in alloy steels),
 - b) thermodynamic and kinetic modeling of interfaces and interface reactions, including 2-dimensional phase equilibria, to predict segregation behavior in multicomponent systems;
- 5) development of theoretical modeling techniques to understand the physics of cohesion and adhesion--for example, how to handle charge transfer/atomic volume effects in developing a theory of intergranular cohesion as a function of composition;
- 6) grain boundary reactions--
- a) develop techniques for studying directly reactions on surfaces and relating them to grain boundaries, i.e., adatom experiments by
 - i) FIM,
 - ii) field desorption,
 - iii) LEED,

- b) determine the relevant impurities in specific alloy systems which are involved in environment/grain boundary interactions such as
 - i) H_2 , H_2S cracking,
 - ii) anodic dissolution, passivation, and re-passivation,
 - iii) liquid metal embrittlement,
- c) determine the mechanisms of these interactions, e.g., H_2 /metalloids and liquid metal/metalloids.

IV. Further recommendations:

- 1) support the development of specific equipment such as those for
 - a) LEED diffractometry,
 - b) high spatial resolution electron diffraction and spectroscopy;
- 2) provide more realistic funding for acquisition and operation of advanced capital equipment;
- 3) recognize the primary role of individual interactions to accomplish research-development-technology information transfer. Hence, programs should be developed which encourage scientists from different disciplines to work together, to meet periodically in small groups, and to develop interpreters who can work at the interfaces between disciplines. Specifically, ERDA should encourage:
 - a) interdisciplinary pairs or small groups,
 - b) small technical meetings or focused topics involving people from different disciplines,
 - c) designation of individuals in the larger laboratories whose major duties would involve interpretation and promotion

- of interaction between various groups,
- d) attendance at technical meetings by active research and development personnel,
- 4) provide funding for travel to and residence at national facilities and structure their use so that these resources can be more effectively utilized.