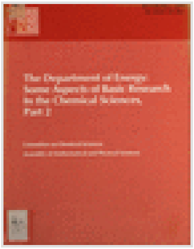

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THE DEPARTMENT OF ENERGY:
SOME ASPECTS OF BASIC RESEARCH IN THE CHEMICAL SCIENCES,
PART 2

COMMITTEE ON CHEMICAL SCIENCES
ASSEMBLY OF MATHEMATICAL AND PHYSICAL SCIENCES
NATIONAL RESEARCH COUNCIL

NATIONAL ACADEMY PRESS
Washington, D.C. 1981

NOTICE

The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Office of Chemistry and Chemical Technology
National Research Council
2101 Constitution Avenue, N.W.
Washington, D.C. 20418

Honorable James B. Edwards
Secretary of Energy
Department of Energy
Washington, D.C. 20585

Dear Mr. Secretary:

I am pleased to transmit the attached report, "The Department of Energy: Some Aspects of Basic Research in the Chemical Sciences, Part 2," prepared by the National Research Council's Committee on Chemical Sciences.

This report, the second of two complementary reports by the Committee on the role and status of chemistry research in DOE (and in its predecessor agency, ERDA), urges an increase in DOE's funding of basic research. Despite greatly broadened responsibilities assigned to DOE, annual expenditures for Basic Energy Sciences (BES), in constant dollars, were lower during 1973-1979 than in 1970-1971 and represent a declining fraction of the Department's total research budget. In a recent report on R&D needs in DOE, the Energy Research Advisory Board (ERAB) also concluded that the support of BES within DOE has been declining and that the long-term health of the energy future of the country requires immediate reversal of this trend. This same concern has now been voiced by three separate groups: the Committee on Chemical Sciences, the OSTP Working Group of Dr. Buchsbaum, and the ERAB R&D Panel of Dr. Bennett.

We are heartened, therefore, by your statement of February 24, 1981 that the Administration intends to refocus government support of energy R&D toward long-term, high-risk activities. We enthusiastically endorse this goal, and hope that, in spite of overall budgetary constraints, funding of basic research in DOE can be restored to levels commensurate with the long-range energy needs of the nation.

Sincerely yours,
Philip Handler
President

June 24, 1981

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* Term expired December 31, 1980
** Term began January 1, 1981

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* Term expired December 31, 1980
** Term began January 1, 1981
***Term expired June 30, 1980

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The Department of Energy: Some Aspects of Basic Research in the Chemical Sciences,

Part 2

INTRODUCTION AND SUMMARY OF RECOMMENDATIONS

This report complements an earlier report (hereafter referred to as Part 1), The Department of Energy: Some Aspects of Basic Research in the Chemical Sciences, issued by the National Research Council's Committee on Chemical Sciences in 1979. The two reports together are a statement of opportunities and needs in the Department of Energy's program of basic research in the chemistry-related sciences, as perceived in 1979-1980 by research specialists in diverse areas of the chemical field. The primary purpose is to assist program officers and administrators of DOE's Office of Basic Energy Sciences (OBES) in examining present and future plans for orienting and expanding the scope of research to meet the Department's broadened responsibilities. Such assistance was requested of the NRC by Dr. James S. Kane, Director of OBES (formerly Director of the predecessor Division of Physical Research in the ERDA), in a letter of January 7, 1977 (Appendix A of Part 1). An auxiliary purpose, served by wide distribution of the two reports, is to engage the interest of research investigators in scientifically intriguing opportunities for basic research germane to the energy needs of the country. As a consequence, the report includes some material likely to be familiar to scientists and agency officials already engaged in energy-related chemical research.

In responding to its charge the Committee has focused on the basic research in chemistry that, in the long range, is likely to contribute significantly to the solution of energy problems. A great deal of such research is already supported to some degree by OBES, industry, or other federal agencies. Because of the complexity of assessing this support, we have made no attempt to indicate where and to what extent it occurs. Our listing of research areas is not to be taken as an indication of a lack of appreciation of current research support by OBES but only as a reflection of the importance the Committee attaches to such research.

The Committee on Chemical Sciences emphasizes that the statement presented in these reports is by no means a complete or final one. Science and technology, along with efforts to meet the nation's energy requirements, are dynamic, on-going enterprises. The sources and utilization of energy particularly are in a transitional state as petroleum reserves dwindle. For some time to come, the civilized world will continue to be primarily dependent on conventional and nonconventional fossil fuels, supplemented by nuclear energy, to meet foreseen needs. These resources must be used as effectively as possible while we look ahead, ultimately to renewable resources. The basic research here recommended is in anticipation of the bridging of that transition. If such advice is to remain useful, it needs review and updating, at suggested intervals of from three to five years.

A. RESEARCH POLICY ISSUES

Spectrum of Research Support: The opening section of this report consists of three chapters addressed to research policy issues crucial to the deployment of OBES resources for basic research in chemistry. The energy technology of the future depends on the research of today. Energy research spans a spectrum from troubleshooting of current processes to basic understanding of the nature of matter. The Department of Energy is concerned with developmental, applied, and basic research, the first two primarily in the technology divisions and the last in the Office of Energy Research (OER). The Committee has not examined the full spectrum of research in parts of DOE other than OBES, but it wishes to encourage the officials guiding the energy technology programs to maintain strong interactions with OBES staff and programs. Efforts by staff members of OBES divisions to interact with staff members of technology divisions have elicited useful responses. Such interactions should be reciprocally maintained and strengthened. Further, the Committee encourages support for relevant basic research by the technology programs. Although overlap of research programs supported by OBES and the technology divisions should be avoided, support of basic research by the technology divisions can help assure that an adequate level of effort is maintained in perceived problem areas. Good communication of the kind sought by OBES will prevent unneeded overlap of research activities and at the same time increase the likelihood of appropriate basic research support by the technology programs. Organizational bridges between the two classes of divisions should be considered.

Within the OBES the spectrum of research still extends from applied to basic research. The problems associated with maintaining an appropriate balance are considered in Chapter 1, "The Spectrum of Research Support." It is pointed out that the more applied research is driven by identified needs. Basic research, on the other hand, has broad and long-range objectives. OBES should encourage first-rate investigators to submit research proposals where the potential relevance to gnergy may be even very broad and long-range; the scientific quality of these proposals should guide the allocation of resources.

The Committee refers readers to Part 1 for its statement of the case for DOE support of basic research and for continuing close interaction between groups involved in basic research, or its support, and those involved in applying to technology the knowledge gained from that research.

Research-Energy Matrix: The Committee found it easy to identify areas of research with strong potential for contributing to the solution of energy problems but experienced great uneasiness on the question of priorities, for two reasons. Priorities for the allocation of research resources require more than a one-dimensional list. One does not eliminate support for an area of research B of lower priority than A but rather supports fewer projects in B than in A. Such relationships are not easily expressible and depend, of course, on the quality of proposals in each area. Secondly, in order to recommend whether increased support should go to a particular area, at the expense of other areas, one must acquire knowledge of the importance and quality of research projects in all of the areas, a feat that the Committee would have found difficult to perform, at least within its time constraints. Furthermore this is the job of the program officers of OBES; the skill and foresight of the program officers are the key to proper judgments, in terms of DOE's long-range mission, in the selection of research proposals to support.

In its struggle with priorities, the Committee did develop a systemization of research problems and areas that it hopes will be useful. This is a matrix of areas of basic research, most of them chemically related, versus energy technologies. For each entry the matrix gives an assessment of the perceived potential impact of that area of basic research on the particular technology--whether low, moderate, high, or none. The chief virtue of the matrix is that it gathers together in a convenient form the potential contributions of each of the disciplinary areas of basic research to each of the technologies of interest to DOE. It should be of help to program officers and planners in deciding where to allocate basic research resources. In the use of the matrix, the column headed "Needs Currently Unforeseen" should not be forgotten. We hope the matrix will also guide and stimulate scientists in making research proposals to DOE. This matrix is a first attempt; the impact factors will be challenged; we hope the scheme will be improved.

Funding of Basic Research: In the closing chapter of this Section I, the funding of basic research is briefly considered. The Committee is dismayed to report that despite the greatly broadened responsibilities assigned to DOE since the petroleum crisis of 1973, the annual spending by OBES during the period 1973-1979 has been lower, in constant dollars, than it was in 1970-1971 and represents a steadily declining fraction of the total DOE research budget. It is difficult to see how OBES can be responding effectively to the long-term energy problems of the nation on a constant-dollar budget smaller than was assigned before the problems were generally recognized.

B. RESEARCH NEEDS

In writing this and the previous report, the Committee was faced with the troublesome problem of how to organize the discussion of basic chemical research needs of DOE. On the one hand, the needs flow from the various existing or potential sources of energy, e.g., coal, oil, solar, etc., but on the other hand chemistry as a science is organized into well-recognized subdisciplines, such as organic, physical, and analytical, which cut across the sources of energy. Both approaches have their strengths and their weaknesses. The Committee has opted for the first approach as the primary organizing theme. Thus, Part 1 included chapters on: Basic Research in Coal Chemistry; Basic Research in Reprocessing of Reactor Fuel and the Disposal of Radioactive Waste. (See Appendix B for Contents of Part 1.) The present report contains chapters dealing with chemically related basic research on: Nonconventional Fossil Fuels Other Than Coal: Shale, Tar Sands, Peat, Enhanced Oil Recovery, and Geopressurized Methane; Alternative Energy Resources: Solar and Biomass Energy, Geothermal Energy, Electrochemical Energy; Nuclear Waste Disposal and Decontamination of Facilities. Compromises with a more disciplinary approach were made, however; Part 1 had chapters on Combustion Science and Analytical Chemistry, subdisciplines that cut across many forms of energy. The present report treats as separate subjects Polymer Chemistry and Catalysis and briefly discusses Organic Chemistry and Separation Processes.

The reason for selecting certain disciplinary areas for special emphasis was their importance in such a variety of energy problems (e.g., catalysis) that they could not be treated coherently in relation to individual "sources" of energy. In some instances, their connections to DOE's mission, while cumulatively significant (e.g., polymers), was not central to a particular problem. The choice of such topics was of course arbitrary and arguable.

With regard to the chapters organized according to sources of energy, the aim has been to give the current technological basis and indicate where research might lead to significant improvements. The Committee and OBES are concerned with basic research that will contribute ultimately to the solution of energy problems and bring forth new ideas leading to new technologies. The purpose of discussing the technological basis is to stimulate ideas for such basic research.

In considering the sources and uses of energy, implicit in the discussion is conservation; more efficient processes and better fuels should lead to reduced energy needs. Broad new insights coming from fundamental thermodynamics may help to foster these ends and assist in combining factors for evaluating overall systems. The concern about the environmental impact of each energy source involves chemistry deeply. The important interdisciplinary problem of quantitatively understanding and, if necessary, avoiding the effects of increasing generation of man-made carbon dioxide deserves mention but transcends the scope of this report; it has been discussed in several recent NAS publications.

A few words are in order on the two disciplinary topics treated at length in the present report. Polymer chemistry and the utilization of polymeric materials are intimately connected with energy development and conservation. The polymer industry at present depends on petroleum and natural gas as major sources of chemical feedstocks, as well as energy. Changes are foreseen, and are in progress, to develop coal as a source of needed hydrocarbons. New polymers of exceptional tensile and impact strength and useful over a wide temperature range have recently been developed by exploitation of structural principles established through basic research. The low densities of polymers, and the endless possibilities of varying their particular structures and properties through chemical modification and through blending of composites, make them versatile materials for a wide range of energy-related applications.

Catalysis has been at the heart of petroleum refining, and yet much remains unknown about the detailed mechanisms of heterogeneous catalytic reactions. The technology is largely empirical. Catalysis is equally important in the chemistry of efficient combustion, in removing undesirable components from combustion products, and in converting coal to gaseous and liquid fuels. Catalytic methods that enable industrial chemical processes to be carried out at close to ambient temperature and pressure save energy as compared with high-temperature conditions. Furthermore, the potential high specificity of catalysts puts a premium on their development for many energy-related uses. Important contributions to understanding catalysis are being made through recent basic research on organometallic coordination complexes and surface chemical physics.

A selected list of recent publications bearing on matters discussed in both reports is presented in Appendix A of this report. Attention is called particularly to the DOE Energy Research Advisory Board's _Interim Report on Research and Development Needs in the Department of Energy (September 5, 1980)_.

C. SPECIFIC CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations drawn from the studies and evaluations described in this report are briefly summarized as follows:

I. RESEARCH POLICY

The Committee on Chemical Sciences offers the following general conclusions and recommendations, based on its examination of the spectrum of chemical research funded by OBES:

- DOE funding in constant dollars for research in the Basic Energy Sciences (BES) has declined since 1972, the year before the oil crisis, and represents a steadily declining fraction of the total DOE research budget, even though BES responsibilities have increased enormously over the same period. In order to meet the long-term energy needs of the nation, basic research in DOE needs to be appreciably expanded, particularly in its Office of Basic Energy Sciences.
- Better support for basic university research is especially needed. Such research would benefit from the continuity of multiyear programs and from larger contract awards.
- DOE should continue to recruit outstanding scientists into its research programs. Their diverse interests will create a natural and changing balance between fields, with reason-

able assurance that the new knowledge generated will ultimately lead to useful applications in the energy field.

II. NONCONVENTIONAL FOSSIL FUELS

Research opportunities related to oil shale, tar sands, or peat utilization address four general classes of problems: characterization of constituents, recovery of synthetic fuels, refining of synthetic crude, and environmental problems.

- Effective utilization of oil shale, tar sands, and peat will require an adequate understanding of what these materials are on a molecular level. Basic research opportunities include characterization of the organic and inorganic constituents including heteroatom determinations and studies of physical structure.
- Current shale-oil recovery processes all involve a pyrolysis step. To improve such processes, further detailed kinetic studies coupled with mechanistic studies are needed to provide better understanding of the oil-producing reactions. Such studies should include measurements of the effects of temperature, heating rate, and pressure. Exploratory work aimed at more efficient nonpyrolytic processes should also be encouraged.
- Fundamental research is needed in the areas of heat and mass transfer as it relates to shale-oil recovery. The goals of this work should include defining accurate transport coefficients that will be useful for mathematical modeling and simulation of shale retorting.
- Basic understanding of the catalytic properties of shale mineral matter could lead to improved retorting methods.
- Raw shale oil requires substantial upgrading before it can be fed to a current-day refinery. New, more-selective chemical methods are needed to remove heteroatoms, particularly nitrogen, from raw shale oil.
- Surface-science techniques, applied to tar sands, may clarify the role of bitumen, water, and inorganics in the matrix.

The overall strategy for environmental research concerning nonconventional fuels should encompass the complete cycle from mining and preparations through transportation, processing, and reclamation. The comprehensive program must address source and emission characterization, assess available control methodology, and identify new technology requirements. Considerable research is needed since there is a general lack of reliable data.

Research opportunities for enhanced recovery of oil and gas relate to the three major technologies used:

1. Surfactant or Micellar Polymer Flooding. Fundamental knowledge of the phase behavior and structure of microemulsions that can be either injected into an oil reservoir or generated *in situ* during the

displacement of crude oil and brine is essential for the design of effective surfactant flooding systems.

Critical areas of research include:

- Phase Behavior Studies--Investigations are needed of the phase behavior of complex mixtures of crude oils, water-soluble polymers, brines, and specialized thermally stable surfactants.
- Microemulsion Structure--Investigations utilizing modern techniques should be encouraged.
- Molecular Structure of Surfactants--Investigations are needed of the interaction energies of the surfactants with various crude oils, brines, and mineral surfaces to determine the optimum structure of the surfactant molecules that will provide both low interfacial tensions and low adsorption.
- Development of New Water-Soluble Polymers--Basic research is needed to develop water-soluble polymers compatible with the specialized microemulsion formulations required for high-temperature, high-salinity applications.

2. Miscible Gas Processes. The principal problem limiting the general applicability of miscible gas processes is the tendency of low-viscosity gases to contact only a small fraction of an oil reservoir.

Additional research is needed in the following areas:

- The development of fundamentally new methods for increasing the reservoir volume contacted by the miscible gas.
- Phase behavior studies of CO_2-crude oil mixtures.

3. Thermal Recovery Processes. As in the case of miscible gas flooding, low sweep efficiencies can be a serious problem in steam flooding.

- Research is needed leading to the development of thermally stable chemical additives to increase steam drive efficiency.

Analyses of a number of brines for the <u>recovery of methane from geopressurized reservoirs</u> suggest that current simplified geochemical models of salinity are inadequate.

- More comprehensive and fundamental studies of the physical and chemical mechanisms affecting the overall brine salinity and brine composition in different geopressured formations are needed.
- Fundamental studies of corrosion and scale formation are needed to deal with these conditions.

III. <u>ALTERNATIVE ENERGY RESOURCES</u>

Areas of basic chemistry research of importance to <u>solar energy</u> are classified within the chapter. They include:

- Studies of new and established semiconductor materials, their properties, and methods of preparation.
- Experimental and theoretical investigations of semiconductor surfaces, surface states, and techniques of surface treatment and modification.
- Design of photocatalytic and photosynthetic systems for the efficient decomposition of water and production of useful chemicals.
- Fundamental studies of the semiconductor-liquid junction and the factors affecting the energetics at the interface and the kinetics of surface reactions.
- Investigations of energy transfer in thin films and other arrays and the design and behavior of sensitizer molecules in energy and electron transfer reactions.

Problem areas limiting utilization of geothermal energy sources, where basic chemical research might contribute, include:

- New drilling materials, logging methods, systems for transmitting logged information, and other devices, adaptable to the high temperatures, high pressures, and hostile environments encountered in deep wells.
- Studies of the hydrothermal behavior of mineral systems encountered at great depths, the phase changes that occur when brines of deep origin are brought to the surface and cooled, and the mechanisms and control of scaling and corrosion encountered in the handling of such brines.
- New systems for the control and utilization of the heat available from various geothermal sources, particularly those at greater depths.
- Theoretical and experimental research on the impact of widespread tapping of geothermal energy on the environment, such as geologic stability, surface-level radiation, and chemical contamination of the atmosphere and of groundwaters.

The important areas of basic research in electrochemistry include:

- Studies of the fundamental factors controlling charge transfer reactions at interfaces and the development of new electrocatalysts.
- Studies of the detailed structure of the electrode surface and of adsorbed reactants and intermediates, including *in situ* methods of investigation.
- Synthesis of new electrode materials such as conductive polymers, organic metals and semiconductors, and modification of electrode surfaces through polymer layers, adsorption, covalent attachment, etc.
- Studies of electrocrystallization phenomena and factors affecting electrode surface morphology during deposition and stripping.

- Investigations of the energetics, kinetics, and mechanisms of potentially useful electrode reactions.

IV. RESEARCH NEEDS IN SELECTED FIELDS

Polymers. Opportunities for basic polymer research that can pay dividends in the energy field include:

- New polymeric materials and composites of high strength and resistance to environmental stresses, such as extreme temperatures and pressures, aggressive chemical conditions, and radiation.
- Improved basic understanding of morphology, adhesion, stability, and structure/strength relationships.
- Better understanding of, and means to monitor, aging phenomena.

Catalysis. Future energy supplies, utilization, and conservation are deeply dependent on the greater and more effective utilization of catalytic processes.

- Oil, coal, and natural gas are expected to remain the principal sources of energy for transportation for many years, but alternate sources for the production of liquid fuels will be even more demanding with respect to use of catalytic processes.
- Homogeneous catalysis will probably not be involved in large-scale upgrading of oils but should find extensive utilization in the production of chemicals and petrochemicals from synthesis gas. It is likely to contribute also to conservation of energy in the chemical process industry.
- Whereas homogeneous catalysis is largely the domain of inorganic and physical organic chemists, heterogeneous catalysis involves input from nearly all facets of chemistry and chemical engineering, from material science, and from surface chemical physics. Thus, in many cases, research on energy conversion processes will be utilizing highly interdisciplinary approaches. Indeed, certain projects are not likely to be successfully attacked except by collaborative efforts.

Organic Chemistry. The vast range of organic chemistry impacts significantly on many interests of DOE. Coal research, synthetic fuels, solar-energy conversion and storage, and photosynthesis are examples of energy-related areas clearly dependent on basic research in organic and particularly physical organic chemistry. Broad support of these fields is necessary.

Separation Processes. Such processes, based on a variety of new or improved techniques, are becoming increasingly important in industrial technology and clearly bear on improving the yield and quality of petroleum-derived products, as well as on energy-efficient extraction methods and control of environmental contaminants.

- Considerable effort has been expended on modeling separation systems, but a strengthened basic research effort is needed on the kinetics, thermodynamics, and structural factors to provide a basis for optimizing performance.

Disposal of Radioactive Wastes. This remains one of the most important obstacles to the utilization of nuclear energy. Intensive research is needed on the adequacy and stability of host materials and on the interaction of stored wastes with the environment.

Decontamination of Plant and Materials Following Nuclear Operations or Accidents is a related problem.

- Research is needed on effective and practical complexing agents for the most dangerous radioactive species. Chemical conditions should be identified that retard the plating out of trace radioactive species in equipment during routine operation and can be applied to extend the useful life of existing nuclear facilities.

SECTION I: Research Policy Issues

1. THE SPECTRUM OF RESEARCH SUPPORT

I. SUMMARY

The various categories of research comprising the full spectrum funded by the Office of Basic Energy Sciences/Division of Chemical Sciences (OBES/DCS) are examined, and several methods of classification are discussed, together with problems associated with maintaining an appropriate balance.

II. CONCLUSIONS AND RECOMMENDATIONS

- OBES as a whole is grossly underfunded.
- The support of basic university research is especially deficient. Such research would benefit from the continuity of multiyear programs and from larger awards.
- The future development and commercialization plans of DOE generate needs for necessary mission-oriented research, and these needs are a major consideration in the allocation of funds for research of this type.
- Fundamental, untargeted research requires no externally imposed balance between energy-related fields. If outstanding scientists are recruited into DOE research, their diverse proclivities will create a natural and changing balance, with reasonable assurance that the new knowledge generated will ultimately lead to useful applications in the energy field.

III. DISCUSSION

In assessing the completeness of coverage of basic research supported by the DCS of the OBES, it is useful to consider the various ways in which research may be classified. The arrays so derived, each a cross-section in a different dimension of the total body of research, provide a multidimensional view of the full spectrum of current research.

A. Basic Research, Applied Research, and Development

One much-used classification distinguishes between Basic and Applied Research. These have been defined by the Department of Energy as follows:

- Basic Research. Systematic, fundamental study directed toward fuller scientific knowledge or understanding of subjects bearing on national energy needs. Efforts to increase knowledge and quantitative understanding of natural phenomena and environment.
- Applied Research. Systematic study directed toward fuller scientific knowledge for direct use in fulfilling specific energy requirements. These efforts are directed toward the solution of problems in the physical, biological, behavioral, social, and engineering sciences that have no clear-cut applicability to specific projects. This includes the technical means of obtaining the knowledge, understanding, and solution.

The line of demarcation between basic and applied research is not sharply drawn, and inevitably there are proposals that could reasonably be classified in either category. In an earlier discussion of this problem (Chapter 5 of Part 1), the Committee recommended that "the broadest possible interpretation should be given" to such phrases as "subjects bearing on National energy needs," in order to avoid concentration on projects having "an obvious relationship to currently known technologies" at the expense of "the expansion of the knowledge base which is needed to develop the energy technologies of the future."

The distinction between research of either type and developmental work is more easily made and presents no particular problem in the selection of proposals for funding by OBES. The DOE definitions of Exploratory Development, Technology Development, and Engineering Development stress the goal of developmental work as a particular application or product, or some concept or element that contributes directly to the realization of a defined goal. Often, the developmental effort uses knowledge and understanding gained from research.

B. Classification by Field

Since basic research in DOE is directed toward "subjects bearing on National energy needs," a listing of areas into which DOE efforts are divided may be informative:

Fossil energy sources (coal, petroleum, gas)
Fossil energy conversion
Energy conservation
Solar energy
Geothermal energy
Biomass
Hydropower
Fusion (magnetic, inertial confinement)
Fission (including breeder reactors, spent fuel storage, waste management, advanced nuclear systems)
Electrical energy systems and storage
Environmental
Basic energy sciences

Advanced technology and assessment
University research support
Advanced isotope separation technology
General science and research (life sciences, high-energy physics,
    nuclear physics)
Atomic-energy defense research and development
Policy analysis and systems studies

With the exception of a few fields for which responsibility for basic research is assumed by other divisions (for example, Resource Applications supports basic research in geothermal and electrical energy systems), the OBES is the primary basic research arm for the efforts of DOE in its various areas of interest. The Divisions within OBES, however, are mainly field-oriented:

Nuclear Science
Materials Science
Advanced Energy Projects
Biological Energy Research and Conservation
Engineering, Mathematical, and Geosciences
Chemical Sciences

Each of the Technology Divisions of DOE should assume responsibility for some research in its field. However, there should be coordination of such research with that of OBES and a recognized mechanism for picking up results of OBES research that can be advantageously applied by the Technology Divisions.

The interests of the DCS potentially impact on those of all the other Divisions within OBES, and, in fact, on all the "subjects bearing on National energy needs" within the purview of DOE.

Because chemistry is a core discipline for all these subjects, DCS is the logical site for locating basic chemical research programs of the "cross-cutting" type recommended by the Research and Development Panel of the Energy Research Advisory Board in its September 1980 Interim Report. Noting that "Many research areas, both basic and applied, cut across DOE energy missions," and "need special attention because they are important to the ultimate success of several programs, but are too large an undertaking for any single program," the Panel Report calls for the establishment of cross-cutting programs in a number of chemistry-related areas: "Fluid dynamics, separation science, instrumentation and control, materials, tribology, robotics, modeling and simulation, surface reactions, chemical kinetics, biological sciences and geoscience." This Committee concurs with the recommendation of the ERAB Panel but notes the need for balancing the funding of such cross-cutting, target-directed programs with the funding of untargeted, externally generated proposals of less immediately perceptible future value to specific energy programs.

C. Appropriate Balances for Basic Research

This type of balance--between projects in support of applied research or development programs and projects that are exploratory in nature or have no obvious relationship to energy projects--is but one of several of concern to OBES and DCS. Research proposals may be classified by several sets of descriptors:

	I	II
A.	Proposal clearly tied to DOE's mission.	Proposal difficult to relate to a specific energy mission.
B.	Shorter-range	Longer-range
C.	Programmatic	Exploratory, untargeted
D.	Suited to DOE laboratories	Suited to extramural or DOE laboratories

However, the above list does not encompass the full spectrum of research types; there is a continuum of those listed and intermediate types.

Proposals of type IA tend to share the other characteristics of column I. They are easily justifiable in terms of the missions of DOE, and they find ready support, often on the basis of urgency as well as need and merit. Proposals best described by the characteristics of column II run greater risk of postponement or underfunding, since, by their very nature, they seem less urgent than those of column I. Nevertheless, DCS/OBES has recognized the need for support of both types of research and should be encouraged to continue to maintain a reasonable balance of support between them.

Only about 20 percent of DCS funding, however, is allocated to extramural (primarily university) laboratories, permitting only one out of five extramural proposals to be accepted for funding (about a third of those considered worthy of support). In its prior report (Part 1), this Committee recommended that additional new funds be made available for support of extramural basic research--enough to permit acceptance of at least one out of three proposals.

The ERAB Panel similarly finds basic research underfunded by DOE. It concludes that:

> "Pressures for near term technological solutions to national energy problems have led to progressive failure in DOE generally to allocate sufficient resources to basic research on which the long range energy future of the nation will depend.
>
> "...A clear example is in Basic Energy Sciences,...where total real dollars for non-goal-oriented basic research have declined by 35% since 1975. This decrease in funding has been further exacerbated because BES has had to assume additional responsibilities without corresponding increases in budget.
>
> "Further, the cost of operating major research facilities (included in BES operating budget) is rising much faster than inflation and the rate of increase of BES budget. This is draining funds

> from real basic research support and important areas of basic research are presently underfunded...
>
> "To restore the funding of basic research in DOE to levels appropriate to the long range energy needs of the nation, [we recommend] increase [of] real dollar funding for Basic Energy Sciences, beginning in FY82, at a minimum rate of 10 percent per year for five years, which will begin to adjust this funding to a level more appropriate to the needs of DOE and the nation. This would amount to an increment of approximately $50M in 1982.
>
> "When new areas of research are added to the BES responsibility in the future, this should be accompanied by sufficient budgetary support above the 10 percent annual increments."

The Committee supports these ERAB recommendations, as well as its statement that

> "...productive basic and applied research requires reasonable constancy of funding to engage the best minds and maintain support facilities. [We recommend that DOE] continue to plan basic research on a three-to-five year budget cycle and commit some portion of the total DOE budget to the implementation of the highest priority multi-year programs."

The Committee further believes that larger research grants by DOE, sufficient to allow meaningful research in the fields involved, would interest more of the most highly qualified academic chemists.

The problems inherent in determining appropriate balances in the research funding allotted by DOE to the various fields within its responsibility, as well as balances between the several types characterized by the descriptors in columns I and II above, are knotty. Further, these balances will change with time, as national commitment to various alternatives for future energy supplies shift with changing sociopolitical viewpoints, with changing economics of the several alternatives, with changes in the state of the art for each, and with the changing needs and resources of our society.

Maintenance of appropriate levels and balances of research support, in the face of all these factors, however, is more a problem for applied research and for mission-oriented basic research (of the type of column I above) than for untargeted basic research (of the column II type). Mission-related energy research, both basic and applied, must be related to the needs of specific developmental, demonstration, and commercial operations. The level of support required must be determined by the judgment of OBES administrative officers, in the light of their assessment of the needs and opportunities presented by emerging divisional programs of DOE, of the probable rate of development of each new energy source, the timing of its introduction and use, and the scale and variety of forms of its adoption. This judgment, based on the experience, knowledge, skill, and imagination of the administrators, and derived in consultation with experts in the technologies involved, must continue to decide the distribution of OBES funds between fields.

Basic energy research of the untargeted type, however, need have no such balances. The directions in which it proceeds, and the energy systems that may ultimately benefit from the knowledge revealed by such research, are perhaps best determined by the natural balance resulting from the interests, the ideas, the imagination, and the instincts of our diverse chemical research community. If DCS/OBES can enlist the participation of outstanding scientists, can assure the selection for support of the best proposals submitted, and can provide continuing support at the levels recommended above, they will have invested the allotted research funds, in the opinion of this Committee, in projects from which will surely flow the energy systems of the future.

2. A RESEARCH-ENERGY MATRIX

The preceding chapter of this report, on the spectrum of research support, discusses the need for a balanced distribution of funds. In making such funding decisions, whether short or long range, it is vital to consider the impact of the proposal on technology. Consideration of such impact implies a priority decision, since funds are limited. To illuminate the impact of such decision-making, a matrix has been designed to provide perspective for assessing the potential impact of chemistry-focused basic, long-range, and pioneering research on energy technology areas. By long-range and pioneering research is meant research undertaken to uncover scientific knowledge that will assist broadly in meeting energy needs over the next several decades.

Chemistry is a ubiquitous science, and categorizing it is an arbitrary exercise. Chemistry disciplines and subdisciplines cross over and blend into one another, and a number of individual classical disciplines are included in each matrix category, as described below. For convenience, the matrix is divided into three technology sections, namely:

I. Fossil Resources--petroleum and related fuels (e.g., tar sands and shale), coal, and petrochemicals.
II. Other Energy Resources--solar, nuclear, biomass, energy storage, etc., as well as an open category labeled "Currently Unforeseen."
III. Environmental Impact

For each of the technology sections, the matrix lists the potential impact--e.g., high or low--of basic, long-range, and pioneering research in the following categories:

AGRICULTURAL CHEMISTRY--R&D involving fertilizer, N-fixation, plant hormones, fermentation, soil chemistry, biochemistry and photosynthesis (from agricultural chemists' viewpoint), etc.

ANALYTICAL METHODS

Characterization Techniques--new or improved analytical tools needed to extend ability to define molecular structure, surface, etc.

Quantitative Analytical Chemistry--new or improved techniques for quantitative data where now deficient or not possible.

ATMOSPHERIC CHEMISTRY--reactions in and effects on atmosphere and also the upper layers, etc.--mostly from pollution and climate viewpoints; includes solid/solid and solid/gas reactions.

CATALYSIS

- Heterogeneous/Homogeneous
- Enzyme/Microbial

CHELATES AND METAL ORGANICS

COMBUSTION

ELECTROCHEMISTRY

EMULSION AND COLLOID CHEMISTRY--includes microemulsions and macroemulsions and suspensions in any fluid medium, liquid surface interactions, foams.

GEOCHEMISTRY

MATERIAL SCIENCE--includes ceramics, composites.

MEMBRANE SCIENCE--includes synthetic, biological, liquid, monolayer assemblies.

NUCLEAR CHEMISTRY

POLYMER SCIENCE

PHOTO SCIENCE--chemistry, physics, and biology; photosynthesis, including work aimed at artificial photosynthesis.

RADIATION CHEMISTRY--includes stimulation of reactions by lasers, electron beam, and other high-energy sources; also, desirable and undesirable effects of nuclear radiation.

REACTION DYNAMICS--physical-organic and physical-inorganic chemistry, reaction mechanism, kinetics, thermodynamics, and to some extent engineering reaction dynamics.

RHEOLOGY

SEPARATION SCIENCE--includes both new and improved analytical techniques, as well as research that could lead to better processes and technology.

SOLID STATE SCIENCE--includes chemistry and physics of the solid state, semiconductor science.

SOLUTION CHEMISTRY--all aspects of reactions involving a solution.

SURFACE CHEMISTRY

SYNTHETIC CHEMISTRY--both inorganic and organic.

THEORETICAL CHEMISTRY--quantum mechanics, statistical mechanics, empirical force field calculations, and other calculational aspects of chemistry.

For the most part, basic, long-range, and pioneering research is generally concentrated in technology areas that are broadly definable in terms of the science and technology of today. But in evaluating the potential impact and relevance of basic research on evolving energy technology, it is important that a truly new idea not be considered irrelevant solely because it does not quite fall into any of the categories listed in the matrix. Accordingly, no negative impact factors are included in the matrix, but rather the impact factor code includes a blank defined as follows:

Blank--potential impact, if any, not perceived at present.
Low--a potential impact perceived.

Moderate--potential impact could be significant.
High--a major impact potential acknowledged.

No impact factors are listed in the column under "New Systems, Processes, Concepts, or Fuels," even though one could visualize a moderate or strong potential impact for several of the research categories. Two examples are H--or high--for enzyme/microbial catalysis and M--or moderate--for membrane science. The column is there as a reminder that many of the fruits of basic research are not discernable when that research is undertaken, and that the recognition and support of new ideas deserves constant attention.

1 Fossil Resources

	Petroleum						Related	Coal					Chemicals	
				Products				Production						
	Enhanced Recovery–Production	More Active/Selective Processes	Low Energy–Separations/Conversions	Lubricants–Lower Friction	Lubricants–Improved Utilization	Fuels–Improved Utilization	Residual Shale, Tar Sands, etc.	Increased Recovery	Transportation/Storage	Cleaning	Direct Combustion	Gasification, Liquefaction, Pyrolysis	More Efficient in Energy and Better Use of Reaction Heat	More Efficient Use of Feedstock
Agricultural Chemistry	L												M	
Analytical Methods														
Characterization Techniques	L	H	M	M	L		H				L	H	L	L
Quantitative Analytical Chemistry	L	L	L	M			M				L		L	L
Atmospheric Chemistry	L					L		M	L		L	L		
Catalysis														
Heterogeneous/Homogeneous		H	H	L	M	M	H			M	L	H	H	H
Enzyme/Microbial	M	H	H				L			L		L	M	L
Chelates and Metal Organics	L	M	M	L	L	M	M				L	L	L	L
Combustion	L		L			H	L	M	L		H	L	M	M
Electrochemistry		M											M	M
Emulsion and Colloid Chemistry	H	L	M	M	M		M		H		L	M		L
Geochemistry	H						H	H						
Material Science	L	L	L	H	H	M	L				M	M	M	L
Membrane Science	L	L	H				L							
Nuclear Chemistry														
Polymer Science	M			M	M								M	M
Photo Science		L											M	
Radiation Chemistry												L		
Reaction Dynamics		M	M	M	M	M	M			L	L	M	L	L
Rheology	H		L	H	H		L		M			M	M	
Separation Science		M	H		M		L				M	M	H	M
Solid State Science	L	M	M	H	H							M	M	M
Solution Chemistry	M		L					L		L		M	H	M
Surface Chemistry	H	M	H	H	M	L	M		L	L		H	M	M
Synthetic Chemistry	H	M	M	H	M	L	M					M	M	M
Theoretical Chemistry														

Impact Factor: Low-L, Moderate-M, High-H; blanks in the table indicate that the potential impact is not now perceived.

II Other Energy Resources

	Solar			Other			Nuclear + Radiochem.						Currently Unforeseen
							Fission Cycle						
	Direct Thermal	Photovoltaic	Photochemical	Biomass	Fuel Cell	High Energy Density Battery	Materials	Isotope Separation	Heat-Generation and Transmission	Fissionable Rec'y Reuse-Inventory	Waste Disposal	Nuclear Fusion	New Systems, Processes, Concepts, or Fuels
Agricultural Chemistry				H						L			
Analytical Methods													
Characterization Techniques	L			L	M	M			L	H	L	M	
Quantitative Analytical Chemistry			L		L	M		M		H	H	M	
Atmospheric Chemistry	M		M										
Catalysis													
Heterogeneous/Homogeneous	L		M	M	H	L							
Enzyme/Microbial			L	H	L			L					
Chelates and Metal Organics				L	L	H	L	H		H	M	L	
Combustion				L	L								
Electrochemistry		H	H		H	H	M	M		L		L	
Emulsion and Colloid Chemistry	L		L		L	L				H		M	
Geochemistry							L			H	H	L	
Material Science	H	H	H		H	H	H	M		L	H	H	
Membrane Science	M	L	M	H	M	M		H		H	L	L	
Nuclear Chemistry							M	M	M	H	H	M	
Polymer Science	H	M		M	M	M						H	
Photo Science													
Chemistry/Physics	H	H	H	M		L		H				H	
Biology			M	H									
Photosynthesis	L	L	M	M				L					
Radiation Chemistry			L				M	H	M	M	M	M	
Reaction Dynamics	L		M	M	M	M		H				L	
Rheology													
Separation Science	H		L	H	M			H		H	H	H	
Solid-State Science	H	H	H		H	H	H		H		H	H	
Solution Chemistry	M		L	L	L	H		H	M	H	H	M	
Surface Chemistry		H	M	L	M	H	H		H			H	
Synthetic Chemistry		L	L	L	L	M				M	H	L	
Theoretical Chemistry		M	M	M	L			H		L			

Impact Factor: Low-L, Moderate-M, High-H; blanks in the table indicate that the potential impact is not now perceived.

III Environmental Impact

	Green House Effect	Pollutants Formation and Control			Toxic Substances	Waste Utilization (Excluding Nuclear Plants)
		Gaseous	Liquid	Solid		
Agricultural Chemistry	M	L	M	M		M
Analytical Methods						
Characterization Techniques	L	H	H	H	H	H
Quantitative Analytical Chemistry	H	M	M	M	H	M
Atmospheric Chemistry	H	H	-M-			
Catalysis						
Heterogeneous/Homogeneous		H	M			L
Enzyme/Microbial	L		L	L		L
Chelates and Metal Organics					M	
Combustion	L	H	H	H		M
Electrochemistry	L	L	M			
Emulsion and Colloid Chemistry						
Geochemistry	H	M	M	M	L	
Material Science		L	L	L		L
Membrane Science	L				M	L
Nuclear Chemistry						
Polymer Science						L
Photo Science						
Chemistry/Physics	M	M				
Biology	M					
Photosynthesis	H					
Radiation Chemistry	H	M	M	M	H	M
Reaction Dynamics	H					
Rheology						
Separation Science	M	M	M	M	M	H
Solid State Science						M
Solution Chemistry	M		M	L	M	L
Surface Chemistry	L					
Synthetic Chemistry						M
Theoretical Chemistry	M	M			L	

Impact Factor: Low-L, Moderate-M, High-H; blanks in the table indicate that the potential impact is not now perceived.

3. FUNDING OF BASIC RESEARCH IN THE DEPARTMENT OF ENERGY

I. CONCLUSION AND RECOMMENDATION

Department of Energy (DOE) funding for research in the Basic Energy Sciences (BES) has declined since the oil crisis in 1973 and represents a steadily declining fraction of the total DOE research budget, even though BES responsibilities have increased enormously over the same period. This is in contrast to the performance of the petroleum industry, which has been spending a steadily increasing fraction of its R&D funds on basic research. In order to meet the long-term energy needs of the nation, it is recommended that basic research funding in DOE be increased, particularly in its Office of Basic Energy Sciences (OBES).

II. DISCUSSION

In an interim report by the Energy Research Advisory Board, it was pointed out that DOE "funding of basic research has been declining and is inadequate to meet the long-term energy needs of the nation. Pressures for near-term technological solutions to national energy problems have led to progressive failure in DOE generally to allocate sufficient resources to basic research."[1] To alleviate this short-coming, recommendations are made in that report to restore basic research funding in DOE to appropriate levels.

As Figure 1 shows, the annual expenditure on Basic Energy Sciences in the period 1973-1979, in constant dollars, is less than it was in 1970-1971. This decline has occurred despite the oil crisis that first became evident in 1973 and the wider range of problems for which DOE is now responsible than its predecessors were earlier. It is difficult to see how OBES could be responding to the long-term energy problems of the United States while operating on a constant-dollar annual budget smaller than it had before the problems were generally perceived. For comparison, the spending for basic research by the petroleum industry, while still below the 1969 level, has shown a dramatic increase--over 50 percent--since 1972.

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[1] Energy Research Advisory Board, Research and Development Panel, Research and Development Needs in the Department of Energy, September 5, 1980.

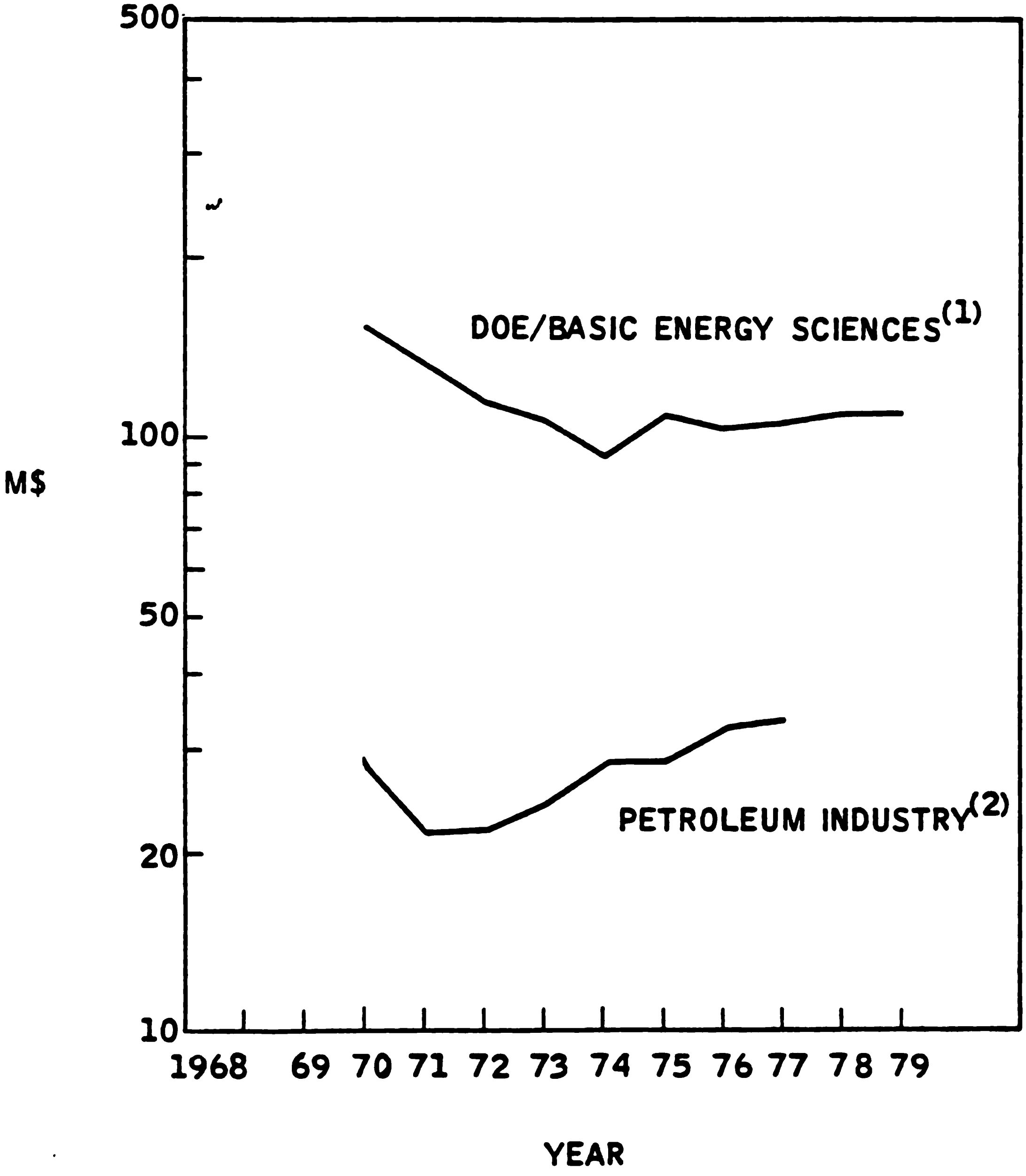

FIGURE 1. Expenditures for basic research (constant 1972 dollars).

Figure 2 shows funding for basic research as a percentage of funding for all DOE research and development. DOE is spending a continually decreasing percentage of its R&D funding on Basic Energy Sciences research (e.g., 10 percent in 1970, 8 percent in 1973, 4 percent in 1979). On the other hand, while petroleum industry percentages must be qualified owing to the method of reporting (see Note 3 for Figures), the industry has consistently increased its percentage of R&D funding for basic research since 1972.

These trends in DOE expenditures are borne out in the types of activities funded in recent years. Generally, DOE has been supporting major pilot-plant demonstrations of laboratory-proven processes, particularly in synthetic fuels. These are primarily development activities, and their extensive funding stands in marked contrast to the agency's ability to support more-fundamental scientific endeavors.

DOE's long-range activities, as exemplified by the OBES budget, have declined and have been a steadily declining fraction of the total budget. The responsibilities of OBES and its predecessors increased enormously in the transition following the 1973 oil crisis, yet the capacity (in funds and resources) to carry out these responsibilities in basic research was never adjusted to the new needs. In contrast, the petroleum industry has traditionally backed up short-range activities with long-range, high-risk, basic research in the hope of establishing major scientific breakthroughs leading to high payout.

No one knows with certainty what is the right balance between long-range basic research and short-range developmental activities, or between public and private sponsorship of research. However, it seems logical that the DOE, a public agency, should lead the way in fostering research whose potential benefits are large, but too general or too long-range to attract support from the private sector. The decline in basic research funding by DOE is a matter of great concern. We believe that an increase in basic research spending in DOE is overdue, particularly in its Office of Basic Energy Sciences.

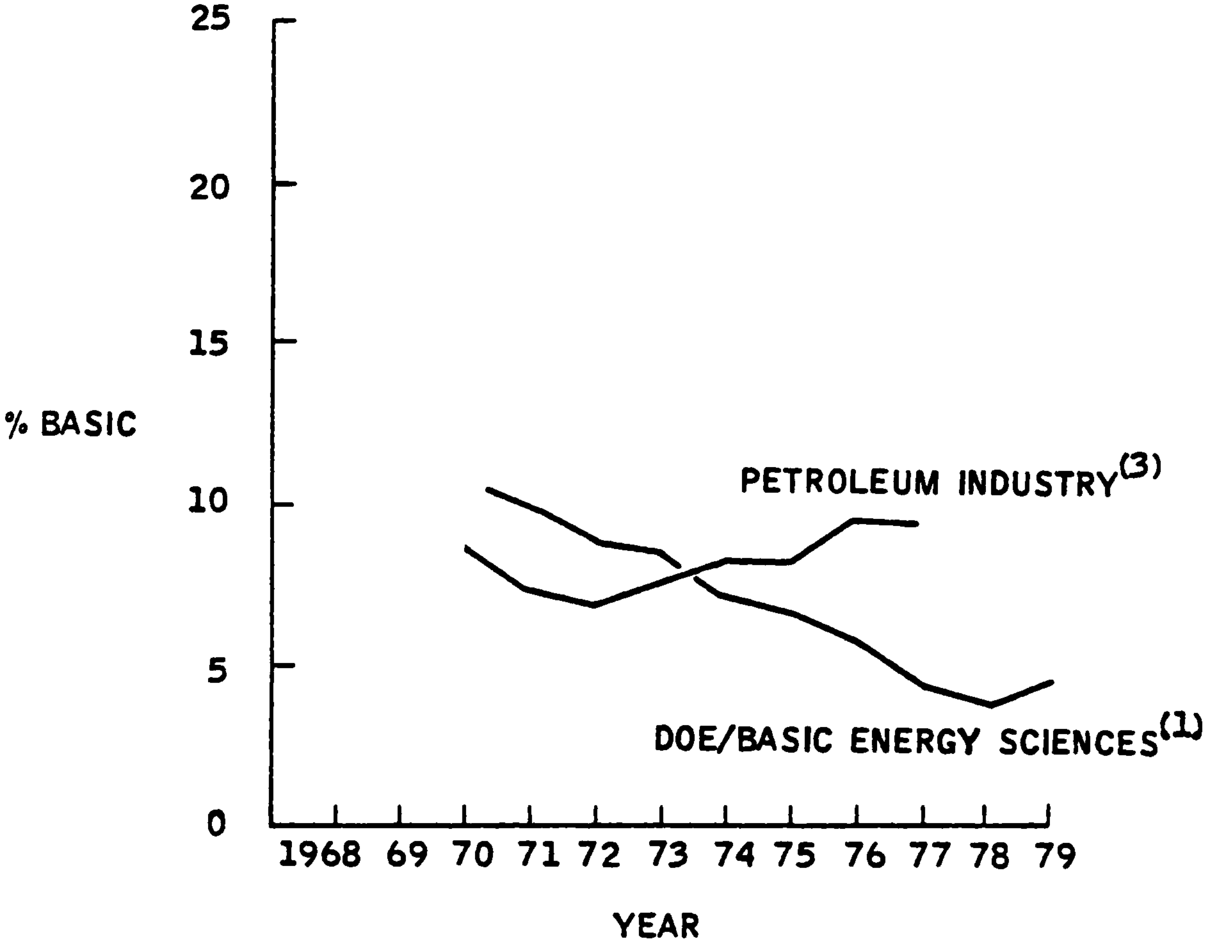

FIGURE 2. Basic research as a percentage of total research.

Notes for Figures 1 and 2

1. E.S. Pierce (DOE), Letter to A. Schriesheim (Exxon Research and Engineering Company), May 1, 1980. Letter provided percents. Dollars were calculated from National Science Board, Science Indicators, 1978, Tables 3-8, 3-9.

2. National Science Foundation, National Patterns of Science and Technology Resources, 1980, Table 42.

3. Percents for Petroleum Industry were calculated by dividing funds for the performance of industrial basic research by industry (NSF, Table 42) by the sum of this plus funds for the performance of applied research and development by product field (NSF, Table 45). Although these funds are not directly comparable (the petroleum industry performs research in many more fields than petroleum products), the NSF, unfortunately, does not publish dollars spent for the performance of applied research and development by industry. Therefore, while actual basic research as a percentage of total petroleum industry research would be lower than the values plotted in Figure 2, we expect the trends to be the same.

SECTION II: Nonconventional Fossil Fuels Other than Coal

4. BASIC RESEARCH IN THE CHEMISTRY OF SHALE, TAR SANDS, AND PEAT

I. INTRODUCTION

The shortfall of petroleum supplies is currently being made up with imports. As this shortfall increases and as the availability of petroleum from secure foreign sources declines, the United States will have to exploit other, but not so convenient, indigenous sources of hydrocarbons. Coal, shale, tar sands, and peat occur in relative abundance in the United States. Their utilization as sources of hydrocarbons is limited by economic and ecologic factors. A new thrust in basic research is required to discover the chemistry that will enable these resources to be utilized effectively. Basic research needed in coal chemistry has been treated in Part 1 and elsewhere (see Appendix A), so this chapter is focused on shale, tar sands, and, to a more limited extent, peat.

The synthetic crude reserves in shale are sufficient to meet U.S. consumption for several centuries at current rates of liquid fuel utilization. Estimates are that 1,800 billion barrels of in-place hydrocarbons are located in the Green River Formation and 2,000 billion barrels in the eastern shales. The U.S. tar sands, while significant in size, are not nearly so large a source of synthetic crude as shale. Estimates are that about 25 billion barrels of in-place hydrocarbons are contained in the Utah tar sands.

Peat, tar sands, and oil shale have an important common characteristic: their energy content on a weight basis is somewhat lower (peat) to much lower (oil shale and tar sands) than that of natural gas, petroleum, and coal. Thus, these fuels will most likely be utilized or upgraded in the vicinity of their occurrence. The highest-grade U.S. deposits of tar sands and oil shale occur in environmentally fragile terrains such as eastern Utah and northwestern Colorado. The relatively high content of mineral matter in tar sands and oil shale and the water in peat are also important factors in selecting the optimum technique for recovering the hydrocarbons. The high proportion of inorganics in oil shale and tar sands presents a disposal problem that generates substantial incentives for *in situ* production of hydrocarbon liquids from these deposits. However, these *in situ* methods are intrinsically less controllable and will inevitably produce lower yields than equivalent *ex situ* recovery procedures. Furthermore, the ability to modify mineral matter to assist in hydrocarbon recovery, and even to recover potentially valuable mineral by-products, is generally reduced for in situ recovery procedures.

The hydrocarbon chemistry of shale oil is similar to that of bitumen and petroleum in terms of carbon/hydrogen ratio and oxygen content, while the hydrocarbon chemistry of peat is closer to that of lignin. Thus, while oil shale and peat both contain high proportions of CS_2-insoluble hydrocarbons, those in shale, namely kerogen, are much more amenable to the production of hydrocarbon liquids than are the woody-lignitic organic constituents of peat. In fact, the similarity of thermally cracked kerogen-derived shale oil to petroleum liquids supports models of the formation of certain natural petroleum liquids via the thermal cracking of kerogen precursors and subsequent migration of the petroleum into a reservoir.

Tar sands and oil shale both pose significant recovery problems. However, there is one important difference: the bitumen of tar sand can be recovered by solvent extraction and upgraded by catalytic processes, while oil shale, owing to its structure, must be thermally treated either in the ground (in situ retorting) or in a reactor (ex situ retorting) in order to recover the bitumen and oil. The thermal reactions that occur during retorting are not specially selective to desired liquid products and produce substantial quantities of char and gas, which are burned for process heat. Furthermore, the retorting process selected may or may not permit the subsequent recovery of potentially valuable mineral constituents, primarily soda and alumina, which occur within the inorganic matrix of certain of the Green River Formation oil shales.

Raw shale oil is the product of the retorting process of western oil shale and, like crude petroleum, is highly paraffinic. But, because it contains higher than normal levels of sulfur, nitrogen, and oxygen as well as olefins and finely divided minerals, it requires substantial upgrading before it can be substituted for refinery feed. Removal of sulfur down to a few parts per million is necessary to protect multimetallic reforming catalysts; however, this technology is well developed for lighter fractions. Removing nitrogen, which also poisons cracking catalysts, from condensed heterocyclic structures currently requires complete ring saturation, calling for the consumption of large quantities of hydrogen.

Peat represents a somewhat different problem since it has a macromolecular structure containing large amounts of oxygen and aromaticity. The types of intramolecular associations and of cross-linking are therefore significantly different from those of oil shale, but the necessity of upgrading peat into smaller molecular species is still of paramount importance. Furthermore, the upgrading of all of these feeds must be done with a high degree of selectivity, or there will be large losses to char and gas of lower value.

II. RESEARCH OPPORTUNITIES

The problems outlined above call for understanding of what oil shale, tar sands, or peat are on a molecular level. The research opportunities discussed below address four general classes of problems: (1) characterization of the organic and inorganic constituents, (2) recovery of synthetic fuels, (3) refining of crude oil, and (4) environmental and toxicological problems associated with substantial production of fuel from these reserves.

The discussion of research problems relating to the three types of hydrocarbon sources under consideration is integrated wherever possible to emphasize common features identified. However, where this approach is not feasible, as in the problem of recovering valuable inorganic by-products from processing Green River Formation oil shale, we have discussed each type of resource separately.

III. OIL SHALE

Oil-shale deposits are located in many countries, including France, Australia, the Soviet Union, China, Brazil, Spain, Germany, and the United States. The most extensive high-grade deposits of oil shale in the United States occur in the Green River Formation in Wyoming, in the Piceance Creek Basin of western Colorado, and the Uinta Basin of eastern Utah.

The mineralogy of the Green River Formation is unusual, quite unlike that of most other oil-shale formations in the United States or elsewhere in the world, and is an important reason why most basic research in shale has concentrated there. Most basic research opportunities relating to U.S. oil-shale deposits are quite specific to the Green River Formation.

The Green River Formation was deposited within a land-locked environment during the Eocene Epoch of the Tertiary Period. The beds, containing large hydrocarbon concentration (25 gallons of oil per ton of shale), are best described as marls, typically containing 40 percent carbonate minerals (principally dolomite and calcite) and only 11 percent clay minerals (principally illite).

A. Chemical Characterization

Present-day analytical techniques will have to be pushed to their limits to obtain the information needed to better understand and to improve current shale, tar sands, and peat conversion processes as well as to generate new technology for utilizing these resources. Though many of the analytical methods have a considerable history of petroleum analytical chemistry to draw upon, major differences between petroleum and these other hydrocarbon sources exist that cannot be easily bridged. Most of the research carried out with petroleum has been on the hydrocarbon (nonpolar) portion of the crude. In shale, just the opposite is the case since all the fractions are likely to have some polar functionality associated with them. Two of the major questions to be addressed are: where are the organic heteroatoms, and how are they bonded into the basic carbon structure? These questions apply to the shale itself as well as to the product slate obtained from shale conversion. Conventional techniques that are available now to answer this question have limitations. Areas of research that will have to be expanded are:

- Separations: Techniques available include chemical and/or solvent separations for functional group analysis, gel permeation chromatogaphy for molecular-weight distributions, gas chromatography (GC) using both packed column and glass capillary for product oil identification and distribution, GC distillation for boiling-point distribution, and high-performance liquid chromatography (LC) for all of the above.
- Elemental Analysis: This is an extremely important technique that though widely used now for petroleum research will need tighter requirements for C, H, N, S, and O than are currently acceptable. Methods to analyze for organic carbon in the presence of carbonate minerals would be useful.
- Mass Spectrometry (MS): Several areas of mass spectrometry can contribute significantly to the overall understanding of shale and shale conversion. Pyrolysis/GC/MS can be an extremely powerful diagnostic tool for examining shale decomposition reactions. Its use could help unravel the basic chemistry of kerogen decomposition. Heavy shale-oil fractions could also be studied. GC/MS is extremely useful for product identification and model compound studies. New areas of mass spectrometry such as coupling of LC with MS or the application of ion cluster techniques are important in exploring molecular weight ranges hitherto not accessible to MS investigation but directly applicable to heavy shale-oil fractions.

B. Physical Characterization

The physical properties of shale and peat should be characterized, for example, by conductivity and other electrical measurements, by scanning electron microscopy (SEM) to study morphology, and by spectroscopic probes covering all available frequencies including new frequencies available through synchrotron light sources. Correlations between the physical properties and conversion behavior could be developed and would be extremely useful in selecting the best shale deposits for a given use.

C. Basic Research Needs

1. Conductivity. These complex systems are extremely difficult to analyze in detail. Model systems of minerals and organics are a useful way to begin. Also, changes in the properties of geological specimens after treatment, such as heating, drying, and the addition of surfactants, offer the opportunity to make different observations. Extensive work has been done in the a.c. conductivity of such systems, and the conductivity behavior at various frequencies often serves as the signature of particular species. The electrochemical study of chemical functionalities also warrants some effort.

2. Optical and SEM Studies. These studies would be useful particularly in establishing differences between extractable and nonextractable organics. Tracing the change in morphology associated with treatments such as retorting would be important. Finally, direct observations of the organics at elevated temperature by hot-stage microscopy could explain how these species behave during retorting.

3. Optical Spectroscopies. A major problem is to determine the ability of the spectroscopy to resolve different types of functionalities in such a complicated collection of organics. Assessment with model systems should be in order. The elegant use of biological markers should be pursued.

4. Magnetic Resonance. For proton NMR studies, many of the same comments made about the conductivity studies apply--model systems are useful, and the effect of treatments must be studied systematically. The ^{13}C NMR work should be expanded to provide a detailed picture of the various chemical forms encountered. ESR studies of carbon radicals in shale and peat--especially after treatments--could provide valuable clues about the conversion process.

D. Pyrolysis

1. Kinetics and Mechanisms of Retorting Reactions. Perhaps the easiest way to recover oil from shale is to heat the oil shale to temperatures between 400°C and 500°C thus converting kerogen into oil, gas, and coke. On a commercial scale, this would be done either *in situ* or in retorts *ex situ*. *In situ* recovery has generally been plagued by two major problems: (1) inability to fracture the shale properly prior to retorting and (2) inability to control the flow of heat as well as product gases and liquids. All the problems associated with *in situ* pyrolysis require primarily field experiments, and we feel that little can be achieved by small-scale laboratory experiments to solve them.

Of the four or five processes investigated for the retorting of mined shale, no one process has been shown to be clearly superior. Several use combustion of residual carbon on spent shale to provide process heat while others recirculate heated solids such as ceramic balls or spent shale. Processes are compared by evaluating, among other things, their recovery of oil as a fraction of Fischer assay. Most retorting processes can recover better than 90 percent of Fischer assay; however, there is little information on the kinetics and mechanisms of oil-producing reactions involved. Experimental work has indicated that the retorting process can be modeled as two first-order and three second-order concurrent reactions as follows:

$$\begin{aligned}
\text{Kerogen} &\xrightarrow{k_1} \text{Bitumen}\\
\text{Bitumen} &\xrightarrow{k_2} \text{Oil/Gas}\\
\text{Kerogen} + \text{Bitumen} &\xrightarrow{k_3} \text{2 Bitumen}\\
\text{Kerogen} + \text{Bitumen} &\xrightarrow{k_4} \text{Oil/Gas} + \text{Bitumen}\\
\text{Kerogen} + \text{Bitumen} &\xrightarrow{k_5} \text{Coke} + \text{Bitumen}
\end{aligned}$$

The fact that an autocatalytic mechanism such as this can simulate the retorting reactions is significant and has many implications for processing. Fundamental research is needed to unravel the reaction mechanisms in detail so as to allow optimization of the yields of desired products. This research is closely tied to structural changes occurring in kerogen as it reacts.

More kinetic than mechanistic work has been done on shale pyrolysis reactions during the past decade. Although kinetic rate data are important in order to design and scale up both *in situ* and *ex situ* retorting processes, we consider that it is far more important to combine kinetic studies with mechanistic studies in order to understand better the oil-producing reactions. The studies should include in detail the effects of temperature, heating rate, and pressure.

E. Upgrading of Primary Products

Raw shale oil, while considerably more like crude petroleum than coal liquids, still requires substantial treatment before it can be sent as an important fraction of crude feed to refineries. Prerefining is necessary to reduce nitrogen and oxygen levels and contamination by finely divided minerals. Prerefining will involve distillation/solids separation, hydrogenation and attendant treatment to remove heteroatoms, and hydrocracking to lower the molecular weight. Research opportunities with the greatest impact are in product quality, heteroatom removal, and molecular-weight reduction.

F. Compatibility/Product Quality

Raw shale oil suffers from many of the same stability and compatibility problems that plague coal pyrolysis liquids. Storage and handling are hampered by its relatively high pour point of 75-80°F compared with -30°F for Arabian Light. Olefins and diolefins may amount to as much as one half of the fraction boiling below 600°F and lead to the formation of gums. Research bearing on these problems include studies of mild catalytic hydrogenation of olefins and diolefins, new techniques for lowering viscosity, and novel surfactants and stabilizers.

1. *Heteroatom Removal.* Raw shale oil typically contains 0.5 to 1 percent oxygen, 0.15 to 1 percent sulfur, and 1.5 to 2 percent nitrogen. While oxygen is of potential concern with regard to product stability, it need not be quantitatively removed. Sulfur and nitrogen

removal must be more complete since their compounds poison some of the catalysts used in refining and the sulfur and nitrogen oxides are pollutants. Thus, a number of problems in heteroatom removal offer challenges to research scientists.

a. Nitrogen: Nitrogen compounds in shale oil are generally categorized as strong bases (quinolines, pyridines, and acridines) or weak bases (indoles, pyrroles, and carbazoles). The strong bases are of considerable concern in acid-catalyzed reactions since they will poison acidic sites. Removal of nitrogen from heterocyclic structures is much more difficult, however, than removal of sulfur. It is well known, for instance, that ring saturation is necessary to remove nitrogen, and considerably more hydrogen is thus consumed than is required to remove the sulfur as well. Research is needed on catalysts for hydrodenitrogenation that will selectively remove nitrogen while consuming less hydrogen. Model compound studies can give considerable mechanistic insight here. Since the basic nitrogen species are the catalyst poisons, they might be removed by liquid-liquid extraction or adsorption/ion-exchange. Little work has been done in these areas, and research might generate viable alternatives to costly hydrotreatment reactions.

b. Sulfur: In raw shale oil, sulfur is distributed in all the boiling range fractions, with a maximum concentration of around 1 percent in the heavy naphtha fraction. In a refinery, this cut is fed to a catalytic reformer to produce gasoline blending stock; however, the reforming catalysts (especially the newer multimetallic catalysts) are sensitive to even small amounts of sulfur. Therefore, sulfur must be removed to levels as low as 1 ppm before shale-oil naphtha can be reformed. Hydrodesulfurization technology is well established, and the process constraints for light feeds are well defined. However, in several areas additional research can make a significant impact, and these are primarily in catalysis. Typically, cobalt-molybdenum or nickel-molybdenum in the form of sulfide supported on γ-alumina is used for hydrodesulfurization. However, these catalysts add hydrogen to the organic structure well in excess of the stoichiometric amount needed when ring saturation of such materials as thiophene or dibenzothiophene is known not to be a prerequisite for removal of sulfur. Research should focus on catalysts that would selectively produce H_2S and butadiene from thiophene, or H_2S and biphenyl from dibenzothiophene, without additional aromatic saturation. Hydrogen saving here could be substantial. Model compound studies and detailed analysis of all products by gas chromatography/ mass spectrometry are necessary in order to understand completely the reaction mechanisms and to facilitate the tailoring of new catalyst systems.

2. Molecular-Weight Reduction. Since raw shale oil is a condensed overhead product of pyrolysis, it does not contain the same kinds of macromolecules found in petroleum and coal residuum. Typically, 95 percent of the raw shale oil nominally boils below 550°C, the residue being mineral matter with some heavy material that was car-

ried overhead. Assuming that the basic nitrogen poisons can be sufficiently removed, conventional catalytic cracking is an efficient technique for molecular-weight reduction. New cracking catalysts more resistant to basic poisons are needed. Molecular-weight reduction can also be accomplished through hydrocracking with a dual-function catalyst, but the problems and opportunities are much the same as described above. Catalyst research should focus on reduction of molecular weight with low consumption of hydrogen.

G. Basic Chemical Engineering Studies Related to Shale

1. Heat and Mass Transfer. Since the major problems of obtaining oil from shale are how to put heat effectively into the shale (either in a retort or in the ground) and release the organic matter trapped within the fine pore structure, it is not surprising that fundamental research is needed on heat and mass transfer as related to shale. The two are not unrelated, and a study of one would necessarily involve the other. For instance, when a shale particle is heated with hot gas, a temperature gradient is established throughout it. This would typically be the case in both retorting and *in situ* recovery processes where particles are relatively large. As the temperature rises, organic (and possible inorganic) matter is released accompanied by an increase in porosity which in turn affects the thermal conductivity and diffusivity. If the heat is applied too fast, coking reactions on the outside of the particle may produce residues, blocking the pores and creating significant resistance to mass transfer out of the particle. These effects are not well understood and merit attention. Research on mass and heat transfer should also strive to produce transport coefficients that can be used in mathematical modeling and simulation of shale retorting, either *in situ* or *ex situ*.

H. Minerals in U.S. Oil Shale

Many unusual carbonate and silicate minerals occur in the Green River Formation, including at least seven minerals first described for this formation. Trona beds [$Na_5(CO_3)(HCO_3)_3$] in Wyoming are currently a major source of soda ash, and nahcolite ($NaHCO_3$), a mineral sometimes associated with Green River Oil Shales in Utah and Colorado, is a potential by-product of oil-shale mining. Dawsonite [($NaAl(CO_3)(OH)_2$)], which is more intimately mixed with certain of the Utah and Colorado oil shales, is an attractive potential source of by-product alumina from oil-shale mining.

I. Research Needs Relating to the Inorganic Mineral Constituents in Oil Shale

Oil shale can be treated in a number of ways to separate its organic and inorganic fractions. *Ex situ* retorting and *in situ* combustion-retorting have received most extensive study to date. In these processes, the shale rock must be fractured on a relatively fine scale to permit efficient heat and mass transfer. Leaching of carbonate minerals by acid or biological agents to accomplish this task provides an alternative to crushing by brute force. Many patents describe such processes, but little literature has been published on which one could base a complete mechanistic picture of the various reactions taking place.

During retorting, temperatures in the vicinity of 500°C are attained, and fundamental questions arise concerning the volatilization of CO_2 from carbonates and H_2O from clays. What reactions between the organic and inorganic constituents take place during pyrolysis, when the inorganic minerals may have a transitorily high surface area? These processes should be carefully studied under highly controlled conditions of time, temperature, and pressure to determine their thermodynamics, kinetics, and mechanics and to evaluate the possibility that the devolatilized inorganic minerals may constitute important catalytic sites for the thermal cracking of the kerogen-hydrocarbon species.

Besides whatever adventitious catalysis might be encountered by appropriate preleaching or devolatilization of certain inorganic constituents of oil shale, such as the carbonate minerals, catalytic species could conceivably be adsorbed onto or intercalated into selected inorganic minerals or their devolatilized products, thereby enhancing the kinetics of kerogen pyrolysis.

Finally, the reactivity and toxic characteristics of retorted oil-shale wastes are a source of concern. The structure and properties of these materials have received little attention so far.

J. Research Opportunities for Mineral Recovery from the Mining of Oil Shale in the Green River Formation

There are many patents on recovery of alumina from Dawsonite-bearing beds by leaching, precipitation, calcining, etc. These concepts need testing on a larger scale. Alumina recovery cannot at present be cited as a credit in oil-shale processing since more work is needed to pin down the economic incentives. Once these are generated, key technical issues that appear to be limiting need to be identified.

K. Characterization of the Inorganic Constituents of Oil Shale

The techniques that have been applied to the characterization of the inorganic constituents in oil shale include x-ray diffraction, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Transmission electron microscopy (TEM) is a powerful tool for detailed identification and morphological characterization of inorganic minerals in fine-grained rocks like coal and oil shale. Techniques of ion milling greatly improve the preparation of TEM samples, and electron energy-loss spectroscopy can now be used for microscopic chemical analyses of the phases encountered.

IV. U.S. TAR SANDS

Oil-impregnated sandstone, commonly called tar sands, occurs on every continent except Australia and Antarctica. The most well-known deposit is the Athabasca tar sands in Canada. Within the United States, 90-95 percent of the tar sands are in Utah. The total deposits there are estimated to be the equivalent of 25.1 billion barrels; 10.8 billion barrels are in the Uinta basin (northwestern Utah) and 14.3 billion barrels are in central southeastern Utah.

The tar-sand reserves in the southeast of Utah are generally located in national parks (Glen Canyon, Lake Powell, Arches), and recovery techniques will need to be particularly sensitive to environmental issues. For DOE-supported research programs, the U.S. tar sands should be regarded as a very small resource compared with coal and oil shale, and they present difficult engineering problems associated with recovery; furthermore, they may require technology carefully adapted to environmental restrictions. Nevertheless, some areas where basic research could contribute to acceptable recovery techniques are described below:

- Characterization: Limited data have been obtained on the characterization of Utah tar-sand bitumen using standard techniques for high-boiling petroleum fractions. This type of analytical study should be extended with emerging characterization tools (^{13}C NMR, mass spectroscopy, functional analysis of heteroatoms, etc.). Many of these techniques have been applied to Athabasca tar-sand bitumen by the Alberta Research Council and University of Alberta. Their application to Utah tar-sand bitumen should provide interesting structural insights since Utah tar-sand bitumen is significantly different in composition from Athabasca tar-sand bitumen and also shows great variation within the deposit (0.14 percent sulfur in Asphalt Ridge versus 4.86 percent sulfur in Southern Triangle).

  Besides research on bitumen characterization, other important areas for characterization research include:

  - Analysis of the Inorganics. This includes such basic information as particle size distribution and its relation to bitumen and water content; analysis should include particles below 44 μm. Also, there has been little analysis of the minerals present beyond quartz. These trace minerals (clays, pyrites, siderites, etc.) can be valuable by-products and often have an important effect on bitumen separation.

  - Role of Water in Utah Tar Sands. The Utah tar sands, unlike the Athabasca tar sands, are believed not to contain predominantly water-wet silica. A useful area of research would be how water is associated with the Utah tar sands. Such research would include surface wetting of oil and inorganics, occurrence of water-in-oil emulsions, water-soluble organic surfactants, and the ionic chemistry associated with the aqueous phase. Understanding the role of water in Utah tar sands could help elucidate why hot-water flotation techniques, which work well with Athabasca tar sands, are generally not effective with the Utah tar sands.

- Matrix Characterization. A difficult but essential part of a characterization program is a description of the structure of bitumen, water, and inorganics in the tar sand matrix. This matrix should be studied by modern experimental techniques. An example would be the freeze-etch SEM procedures developed at the University of Minnesota for the study of microemulsion structure in porous media. Other surface-science techniques could be used, for example, to examine the chemisorption of various bitumen constituents by the inorganics.

- Separation of Bitumen from the Tar Sands. The separation of bitumen from Utah tar sands should be viewed as a specific example of the more general problem of solid-liquid separations. Solid-liquid separations for systems containing heavy hydrocarbons is becoming increasingly important, and their development affects various technologies including the utilization of coal and shale oil. Among areas of interest where the fundamental principles are poorly understood is:

  <u>Flotation</u>. The technological goal is to apply the flotation process used for Athabascar tar sands to Utah tar sands. This probably cannot be economically accomplished by a purely empirical approach. What is needed is an analysis of the solid-liquid-air interface in the tar-sand system. Many of the research areas bearing on bitumen flotation in tar-sands systems are also important for flotation of minerals; a recent workshop sponsored by the Department of Energy outlined important research areas for the flotation of minerals. In summary, scientific programs on tar-sand bitumen flotation can be viewed as a part of research on the beneficiation of minerals.

o In situ Recovery: Environmental and geological factors suggest that a significant fraction of the Utah tar sands would need to be recovered by in situ techniques. In situ combustion processes have been investigated for the deposit at Asphalt Ridge. These tests, and similar ones by several oil companies, have clearly demonstrated the need for more basic understanding of the in situ combustion process. Some of the important areas for research are:

-- Modeling of the Combustion Process. The studies should include heat and mass transfer effects besides the reaction kinetics. Such research can suggest desired techniques to fracture the formation, preferred ranges of gas velocities, etc.

-- Role of Mist Formation. The vapor-phase velocity in combustion processes is much greater than the speed of the combustion front. This difference produces a steep temperature profile and can lead to the formation of an oil mist, which can condense on the sand and undergo further cracking to produce coke; the mist can also drain countercurrent to the gas and thus change vapor-phase flow patterns. The role of mist formation is important for in situ recovery of oil from Utah tar sands and also from shale. Research should aim to relate the rate of mist deposition to droplet size, porosity of the formation, flow rate, holdup of oil, and other related parameters. A combination of theoretical and experimental studies should provide an understanding of the major mechanisms associated with mist deposition.

-- Thermodynamics and Fluid Mechanics of Multiphase Flow in Porous Media. This area of basic study includes the role of capillary forces, emulsification, and the flow of multiple phases (emulsions, gas-liquid) through the porous media.

Basic research relevant to tar sands should focus on problems generally bearing on fossil-fuel utilization rather than developmental problems highly specific to U.S. tar sands. The greatest emphasis should be on characterization, solid-liquid separations, and increased understanding of factors involved in in situ pyrolysis.

V. ENVIRONMENTAL RESEARCH

The overall strategy for environmental control should encompass the complete fuel cycle including mining, preparation, processing, reclamation, and transportation. The comprehensive program must address source and emission characterization, assess available control methodology, and identify new technology requirements.

In general, considerable research is needed in view of lack of data. This research should include:

A. Mining Operations

The major concern associated with mining operations is the fugitive dust emitted from quarrying, hauling, and handling. It is desirable to estimate respirable dust fractions and assess associated health risks. In the past, emission factors have been estimated from similar quarry operations. Values reported by various investigators are in poor agreement. Accurate data are needed to quantify emissions in order to secure environmental permits. Furthermore, the concentration of trace elements and toxic substances in the respirable dust fraction is of considerable concern.

B. Preparation Operations

Such operations as crushing, sizing, transfer conveying, vehicular traffic, and wind erosion are sources of fugitive dust. The dust emission factors are of particular interest in order to estimate emissions and calculate fenceline concentrations, thereby setting the required plant size. They are also of interest in order to evaluate efficiency of various dust control measures such as wet sprays and chemical bonding agents. A major study is required to quantify and model controlled emissions as required by air-quality regulations.

Characteristics of waste water from cleaning operations must be determined for selection of suitable treatment processes and disposal.

C. Processing Operations

Characterization of gaseous emissions such as H_2S, NH_3, CO, NO_x, SO_2, and trace metals is necessary to define their potential for pollution. Such information would help in developing appropriate control techniques to meet air-quality regulations.

Measurement and characterization of particulate emissions must be conducted. The respirable fraction of this particulate matter may be particularly hazardous and may require special control and handling techniques.

Analysis of liquid effluent stream for dissolved solids, ammonia, H_2S, Cl^-, cyanides (CN^-, metal cyanides), SCN^-, organic compounds, polynuclear aromatics (PNA's), and trace metals is required. Suitable waste treatment processes should then be developed to meet the effluent discharge regulations.

D. Products

The carcinogenic potential of fractions (PNA's, etc.) between 550°C and 700°C, intermediates, by-products, and waste effluents needs to be assessed. Presence of carcinogenic substances would necessitate special handling and control measures.

Emissions from combustion of shale oil and other synthetics should be evaluated. Analysis of these emissions and a better understanding of their combustion processes should give clues to reducing undesirable emissions.

E. Reclamation and Solids Disposal

Characterization of solid-waste effluents for PNA's, trace metals, and organics is necessary. Tests on leaching of solid wastes should be conducted to identify potential problem areas.

Trace metal and organic analysis of runoffs and leachates from disposal sites are needed. Physical and chemical aspects of leaching of spent shale should be investigated, including the effects of permeability, pH, and chemical constituents on the leaching mechanism.

Revegetation and stabilization studies of residues is desirable. Spent shale could pose severe chemical problems because of high alkalinity, low organic content, and low levels of plant nutrients. Revegetation with nitrogen-fixing plants is a promising approach. Attempts to add topsoil are hampered by capillary rise of salts into it, thereby affecting plant growth. Currently, few chemical bonding agents are available for control of erosion.

F. In Situ Methods

Retorting of oil shale in situ requires that the H_2S present in the gas phase be converted to SO_2 at temperatures below 300°C. The oil shale acts as an oxidation catalyst in this conversion reaction. However, the catalytic effect is vulnerable to deactivation by water and excess O_2. Little is known about the reaction kinetics of these processes.

G. Cooling Tower

In western states, owing to water scarcity, some process streams might be cooled in towers. This would require characterization of organics and trace metals in cooling water and blowdown.

H. Reuse of Waste Water

Effluent streams from specific processes would have varying degrees of contaminants such as phenols, organic matter, ammonia, and dissolved solids. Methods to characterize contaminants and new methods of treating waste water are needed to meet effluent discharge regulations governing fitness for reuse.

I. General Health and Safety

Methods of assessing health risks associated with respirable dust and toxicological effects of intermediates, by-products, and combustion products are needed to identify potential health hazards.

J. Impact of Synthetic Fuels on the Growth of Atmospheric Carbon Dioxide

A reasonable extrapolation of World Energy Conference and CONAES energy scenarios suggests that a doubling of CO_2 in the atmosphere will occur by about 2070 if the global carbon system responds linearly to the increased quantities of CO_2 that will enter the atmosphere. The contribution of biomass to atmospheric CO_2 was neglected in this estimate. A global synthetic fuels industry was projected to contribute 15-24 percent of the total CO_2 retained in the atmosphere between 1985 and 2070 while providing 29-48 percent of the world's fossil-fuel energy needs in 2070.

Concern about increase in atmospheric CO_2 centers around the property of CO_2 to absorb infrared radiation, while being almost transparent to visible and ultraviolet radiation. Thus, there is speculation that as CO_2 builds up in the atmosphere from fossil-fuel utilization and other sources, it will act as a shield to prevent the radiation of heat into space (i.e., act as a global greenhouse) and cause surface warming of the planet. The climatic effects are discussed in a recent report, Carbon Dioxide and Climate: A Scientific Assessment, Climate Research Board, National Academy of Sciences, 1979. For a review of research needed in this area, see Environmental and Societal Consequences of a Possible CO_2-Induced Climate Change: A Research Agenda, a report prepared for DOE by the AAAS in 1981.

5. BASIC RESEARCH IN THE CHEMISTRY OF ENHANCED OIL RECOVERY

I. INTRODUCTION

The continuing decline in production rates and proved reserves of petroleum and natural gas has stimulated more rapid development by industry of enhanced recovery methods. These methods have the potential of recovering oil that remains in the ground in conventional practices.

The best-known studies of potential future additions to U.S. oil reserves through Enhanced Oil Recovery (EOR) techniques are those by the National Petroleum Council (NPC)[1] and the Office of Technology Assessment (OTA)[2] of the U.S. Congress. In both, estimates made for a selected reservoir data base were extrapolated to give projections of ultimate incremental recovery and potential production rates for currently known U.S. fields in the lower 48 states.

Figure 3 shows the NPC base case projections of incremental ultimate recovery. Values are given as a function of oil price, expressed in 1976 dollars, for projects achieving at least a 10 percent rate of return. The contribution from surfactant, polymer, and alkaline water flooding ranges from less than a billion barrels at $10* per barrel to 8.4 billion barrels (0.16 billion to 1.33 billion cubic meters) at $25* per barrel. Corresponding estimates of recovery by CO_2-miscible processes range from 3.2 billion to 7.3 billion barrels (0.5 billion to 1.16 billion cubic meters). Thermal methods could recover an incremental 7.4 billion barrels (1.17 billion cubic meters) of heavy crude at $25 per barrel if the NPC projections are correct. Recoveries from polymer and alkaline water flooding will be low and relatively insensitive to price.

Figure 4 compares total recovery levels projected by the NPC and OTA. Although the OTA values are, on average, considerably higher than those of the NPC, the range of uncertainty is large for both studies. These uncertainties arise because assumptions made about future developments in EOR technology may or may not be realized, because of uncertainties in crude-price forecasts, environmental restrictions, material supply constraints, and costs, and because of the lack of detailed

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*Based on Consumer Price Index values for 1976 and 1980, oil prices corresponding to $10/bbl and $25/bbl have increased to approximately $14.50/bbl and $36.20/bbl exclusive of the Windfall Profits Tax.

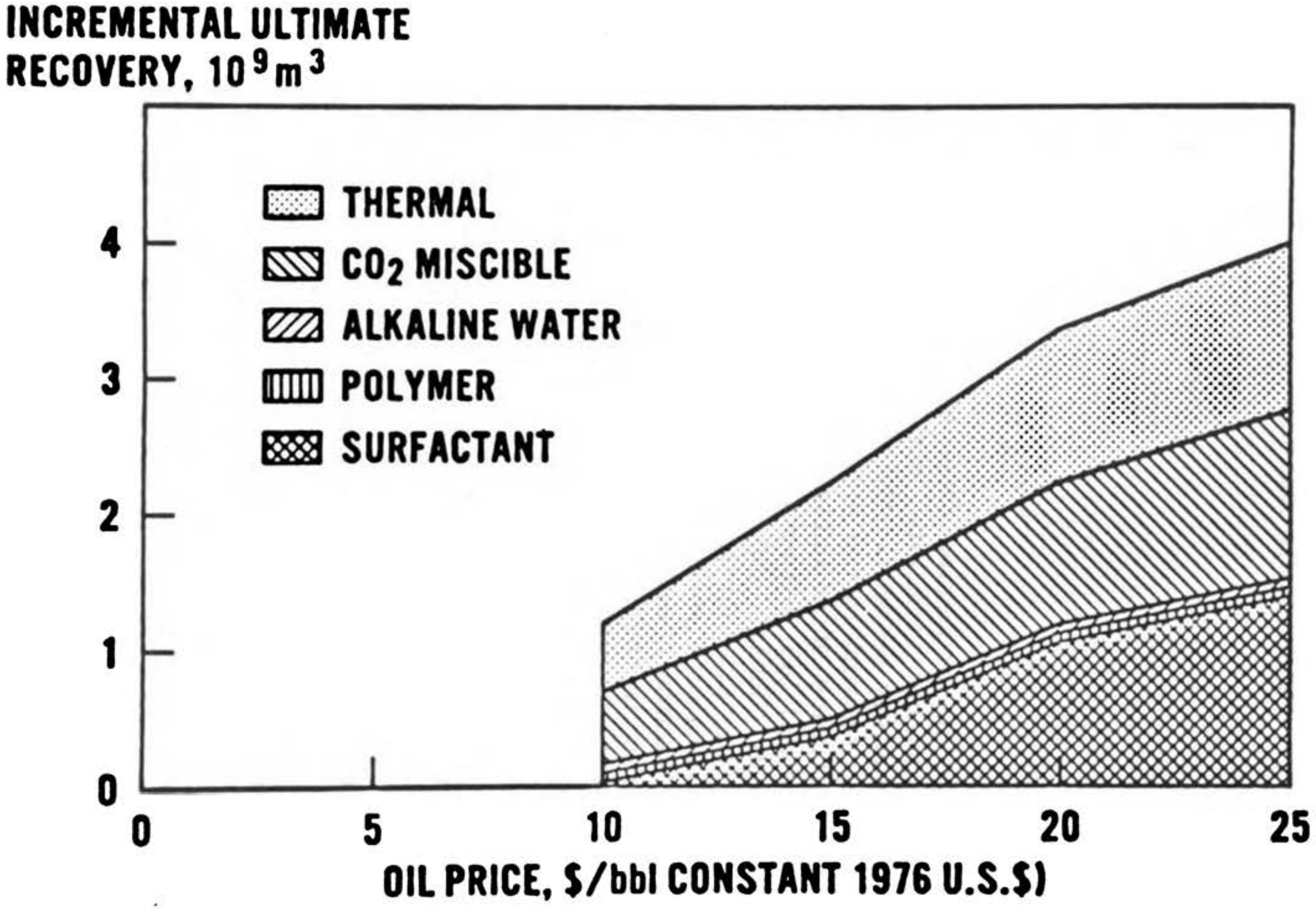

FIGURE 3. NPC base case projections of incremental recovery.

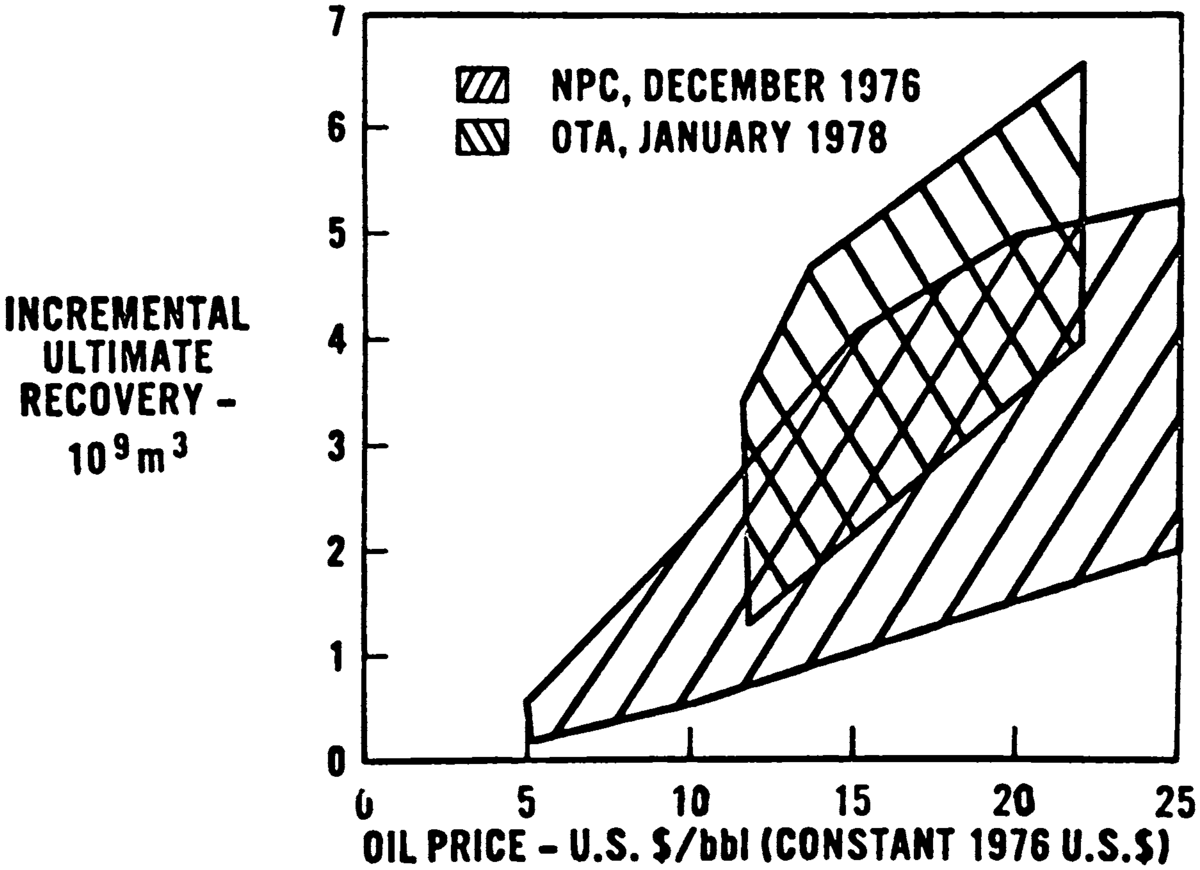

FIGURE 4. Comparison of total recovery levels projected by NPC and OTA.

information concerning reservoir geology and the distribution of the oil that will be left by conventional oil recovery processes.

Although these uncertainties prevent precise estimates of the incremental recovery possible, enhanced oil-recovery methods have the potential of producing an incremental volume of oil approximately equal to current U.S. reserves--that is, the volume of oil that can be recovered from known reservoirs in the United States by conventional methods. Consequently, a comprehensive research program should be undertaken to develop the EOR technology needed to recover this valuable resource.

Conventional oil-recovery practices involve the use of water and/or gas to displace the oil from the reservoir. There are three reasons why a significant fraction of the original volume of oil contained in a reservoir may be unrecoverable by these means:

- First, the fraction of the volume of the reservoir rock accessible to water and gas depends on the geological complexity of the formation and other factors affecting the conformance of the displacement process to the volume.
- Second, not all of the oil can be displaced from the contacted region. Even in those parts of the reservoir that are effectively swept, some oil is left behind with greatly reduced mobility or as immobile oil, trapped on a microscopic scale in the pores of the rock.
- Finally, much of the world's heavy crude is too viscous to flow to a producing well at commercially feasible rates.

The following discussion of these problems provides background for understanding why oil is left in the ground by conventional recovery processes and how trapped, residual oil can be mobilized and recovered by enhanced recovery processes.

Several factors influence the volume of reservoir contacted by injected fluids. As mentioned above, sweep is reduced by reservoir heterogeneities that can make some portions of the reservoir inaccessible to the injected fluids. In other areas the displacing fluid, taking the path of least resistance, may channel through more permeable strata. Geometric effects introduce still another type of problem: "corners" or areas near stagnation points that exist in a typical pattern of injection in producing wells and may be difficult to "sweep." Viscous fingering is a phenomenon that occurs whenever the injected fluid is more mobile (less viscous) than the oil; consequently, the injected fluid tends to bypass oil-bearing zones. Recovery of this bypassed oil may require injection of excessively large volumes of fluid and be impractical. Severe viscous fingering can lead to large reductions in sweep efficiency.

In some reservoirs, the fraction contacted (hence the volume of oil produced) can be increased, for any given volume of water injected, by addition of polymers that decrease water mobility in the pore spaces of the reservoir rock. Thus, an area of chemical research with high potential is the development of new, cost-effective polymers capable of providing the required reduction in mobility for long periods of time (10 to 15 years) in highly saline brine and at elevated temperatures.

Oil is not completely displaced from regions swept by water. Twenty-five to fifty percent of the original oil may remain trapped in most reservoir rocks, even after flushing with large volumes of water. The residual oil is trapped by capillary forces as small, discontinuous, microscopic droplets. Four thousand of these droplets could fit on the head of a pin. If a surfactant solution is injected to lower the normal interfacial tension between water and crude oil by a factor of at least 10,000, the capillary forces holding the trapped oil are reduced, the droplets are able to deform, and they escape, eventually, by coalescing to form a continuous, flowing oil phase.

Of course, another way to remove the trapped oil is to dissolve it. In this case, the interfacial tension goes to zero--the interface disappears--and the oil can be displaced completely in those regions that are swept. The so-called "miscible-gas processes" utilize this mechanism.

Thick or highly viscous and therefore relatively immobile heavy oils present a different problem. In some cases, these crudes will not flow at commercially acceptable rates unless their viscosity is reduced by several orders of magnitude. Typically, this can be accomplished by raising the temperature of the oil 100-200°C. Heating a heavy oil reservoir has proven to be a practical approach to recovery.

II. CONCLUSIONS AND RECOMMENDATIONS

A. Surfactant or Micellar Polymer Flooding

Fundamental knowledge of the phase behavior and structure of microemulsions, which can either be injected into an oil reservoir or generated *in situ* during the displacement of crude oil and brine, is essential for the design of effective surfactant flooding systems for the enhanced recovery of oil. Basic information is particularly needed on systems that can be used in reservoirs at 50°C to 125°C that contain high-salinity brines, that is, brines containing 50 to 200,000 ppm total dissolved solids including several thousand ppm of divalent cations.

Critical areas of research include:

- Phase Behavior Studies. Research should be supported on the phase behavior of complex mixtures of hydrocarbons (simulating various crude-oil mixtures), water-soluble polymers, high-salinity brines, and specialized thermally stable surfactants for use at reservoir temperatures above 50°C. Studies should result in better methods for characterizing crude oils in terms of the types of surfactants needed for EOR applications and for designing molecular structures required for the surfactant and co-surfactant molecules.
- Microemulsion Structure. Microemulsions are extremely stable micellar suspensions of oil, water, and surfactants. Research on the structure of the various types of microemulsion

systems, particularly the "middle-phase" microemulsions frequently observed in the more effective surfactant floods, merits support.

- <u>Molecular Structure of Surfactants</u>. Thermally stable surfactant systems are needed that are capable of maintaining (1) low interfacial tensions and (2) low adsorption losses of the surfactants on rock surfaces. Fundamental investigations should be encouraged that will help to define the optimum structure of surfactant molecules for both low interfacial tension and low adsorption.
- <u>Techniques of Chemical Analysis</u>. Better analytical procedures are needed for fast, precise measurement of the concentrations of different types of surfactants and co-surfactants commonly employed in micellar-polymer floods. Support should be given to the development of new analytical techniques that will expedite acquisition of the data needed to observe critical phenomena occurring during surfactant floods.
- <u>New Water-Soluble Polymers</u>. The general lack of effective water-soluble polymers compatible with the specialized microemulsion formulations required for high-temperature, high-salinity EOR applications is a serious constraint on the use of micellar-polymer systems. Support should be given to the development of low-cost, thermally stable, and shear-resistant polymers. Support should be given also to studies designed to determine the thermal degradation mechanisms and to quantify the conditions required for thermal stability.

B. <u>Miscible Gas Processes</u>

The principal problem limiting the general applicability of miscible gas processes is the tendency of gases with low viscosity, hence high mobility, to contact only a small fraction of an oil reservoir.

Research is needed in the following areas:

- New methods, e.g., use of "foams," for increasing the reservoir volume contacted by the miscible gas.
- Phase behavior of CO_2-crude oil mixtures.

C. <u>Thermal Recovery Processes</u>

As in the case of miscible gas flooding, low sweep efficiencies can be a serious problem in steam flooding.

The principal area of chemical research needed is:

- The development of thermally stable surfactants and polymers or other chemical additives to increase steam drive efficiency.

III. DISCUSSION

A. Surfactant Flooding Processes

Surfactant flooding refers to a group of similar recovery processes all of which use surfactants to reduce the capillary forces that normally entrap the oil in the pore spaces of the rocks. Micellar-polymer flooding, soluble-oil flooding, low-tension water flooding, and microemulsion flooding make up a partial list of typical processes in this group. All of these processes involve the use of stable microscopic dispersions of oil, water, and surfactant called "microemulsions."

Several technical problems remain that either limit the applicability of surfactant flooding or contribute to the marginal economics and high risk associated with the process. First, chemical systems have not yet been fully developed that are useful at the temperatures and salinities encountered in the majority of light oil reservoirs. Second, chemical losses through adsorption and trapping dictate chemical requirements and therefore strongly influence economics. Typically, about 15 to 20 pounds of surfactant per barrel of incremental oil recovered will be lost by adsorption on the rock surface or entrapment within the porous structure.

The temperature-salinity problem can be placed in perspective through Figure 5, which shows conditions for past and ongoing field tests on a temperature-salinity grid. Most field tests have been conducted in low-salinity, low-temperature reservoirs simply because these are the easiest targets. The two most successful tests conducted to date fall within this low-temperature, low-salinity region. Few tests have been conducted in reservoirs with temperatures above 50°C and water salinities greater than 5 total percent dissolved solids. The low-temperature, low-salinity region on this chart represents less than 15 percent of the ultimate potential reserves from surfactant flooding in the United States, while the high-temperature, high-salinity region represents about 50 percent. Thus, the need to develop processes applicable within the upper right-hand section of this grid is apparent.

At reservoir temperatures above 50-65°C, many common types of surfactants degrade over the 5- to 10-year life of a field flood. Surfactant systems exist that should be effective in hot (over 100°C) reservoirs with water salinities less than or comparable with water. However, new surfactants with greater thermal stability are needed, particularly for those applications also involving high-salinity resident brines (e.g., 75-100,000 ppm total dissolved solids). High salinity is a problem because common surfactants that are effective at low salinities are not effective at high salinities. It has proven to be difficult to design and manufacture the specialized, yet cost-effective, surfactant molecules needed for applications at high salinity.

The basic requirements that must be satisfied by the surfactant system are as follows. The system must:

1. maintain low interfacial tension (less than about 5×10^{-3} dyne/cm) at both the front and back of the surfactant bank (a) as it mixes with crude oil and brine ahead of the in-

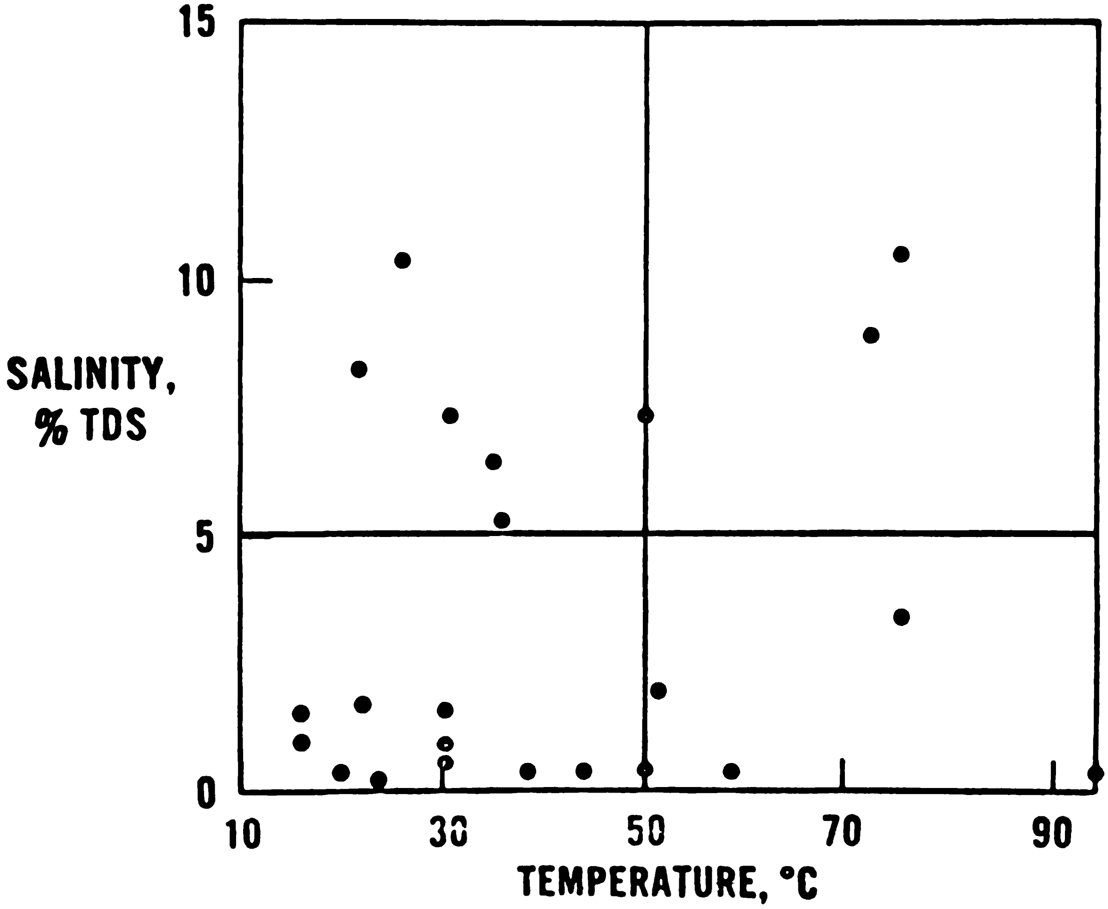

FIGURE 5. Surfactant field activity.

jected microemulsion system and (b) as it is displaced by the viscous (polymer-water) bank at its back end,

2. have low retention of the surfactant system components by either adsorption or immiscible entrapment of the surfactant itself (as the result of poor phase behavior) when it mixes with polymer-water,
3. maintain an effective composition, despite adsorption losses or chromatographic separation of its components as it moves through the reservoir, and, in many applications,
4. maintain good mobility control throughout the flood in order to contact as much of the reservoir as practically possible,
5. withstand thermal degradation throughout the 5-10 year life of a field flood,
6. be tolerant of high-salinity brines that frequently contain appreciable concentrations of divalent ions, and
7. be cost effective (net surfactant losses by adsorption alone on the high surface areas of most reservoir rocks will preclude use of expensive surfactants in the microemulsion).

Many different areas of surfactant flooding technology are fertile grounds for research. These include:

1. Phase Behavior Studies. Systematic studies are needed of the interaction of various types of crude oils, especially those containing colloidal dispersions of asphaltenes, high concentrations of high-molecular-weight naphthenes, paraffins, etc., with surfactants having different structures for the oleophilic portion of the surfactant molecule. Since solubilization coefficients and interfacial tensions are closely related to the phase behavior of oil-water-surfactant systems, research to improve basic understanding of this relationship is needed and could lead to improved surfactant structures. One of the basic problems is the connection between micellar structures and bulk interfacial tensions. A better understanding is also needed of the equilibria believed to exist among the various phases in a microemulsion.

   Considerable progress has been made in unraveling the roles of the various chemical components in determining phase behavior, but much remains to be done. The role of alcohols as cosolvents remains obscure. The intimate involvement of electrolytes in electrical double-layer structures also merits further investigation. The principles for characterizing complex hydrocarbon mixtures are still not clear. Further insight is needed into the collective partitioning of the components of complex mixtures of surfactants, cosurfactants, and cosolvent species and the various constituents of crude oils and reservoir brines. Limits to collective partitioning for sufficiently disparate surfactant and oil phase species are known to exist but have not been defined adequately.

Finally, despite all the effort in recent years, the extant data base is much too narrow--the spectrum of cosolvents, head group polarities and structures, hydrophobe structures, oil-phase compositions, and electrolytes needs to be greatly expanded. The basic knowledge accrued will be extremely valuable in many different areas of technology because of the pervasiveness of surfactants in applications quite removed from enhanced oil recovery.

2. Studies of Microemulsion Structures. Recent experimental and theoretical studies support the view that microemulsions (more properly, micellar solutions) are thermodynamically stable suspensions of oil solubilized in water (water external or Winsor Type I), the inverse (Winsor Type II), or complex middle-phase systems (Winsor Type III), which often contain nearly equal quantities of water and oil. All of these systems can be generated with the simplest of surfactant species by modifying the solvent properties of the various phases. There is irrefutable evidence that very simple systems can form a rich array of structures, varying probably from classicial spherical micelles to truly macroscopic liquid crystals. Yet for any given system it is difficult to obtain a totally unambiguous characterization of structure. Currently, there is controversy regarding the existence of spherical, ellipsoidal (both prolate and oblate), and cylindrical moities even in aqueous surfactant systems containing only two components.

   Additional information is also needed relating shear-dependent viscosity data to the structure of many different kinds of microemulsions. These rheological data are required in determining if a particular type of microemulsion has potential for enhanced oil recovery and in designing microemulsion systems for specific applications.

   Such modern techniques as low-angle neutron and x-ray scattering and dynamic light scattering should be applied to determining the actual structures of complex microemulsions, especially the middle-phase systems, which have proved to be particularly effective for surfactant flooding. The data should aid the development of improved, possibly new, theories of micellar structure.

3. Molecular Structure of Surfactants. An ideal surfactant system must (a) maintain low interfacial tensions and (b) have low adsorption losses of the surfactants on the large surface area contained within the porous reservoir rock. The ideal structure of the surfactant molecule cannot currently be specified for all possible conditions of interest. Much is known of how the structure of surfactant molecules, interfacial tensions, and adsorption are related, but many questions remain unanswered. For example, why does the branching of the lipophile so greatly affect surfactant par-

titioning? What is the origin of the stoichiometric relationship between the size and nature of the lipophile and the molecular structure of the oil phase? What is the origin of the apparent close coupling of the size of lipophile side chains to solubilization and interfacial tensions? Are there effective surfactant structures that are inherently insensitive to electrolyte concentration and composition? And why? How does surfactant structure affect adsorption on metal oxides and clays? In some instances, surfactant systems satisfying optimum conditions in laboratory-phase behavior studies also satisfy conditions of minimum adsorption in porous media. Whether or not this observation is generally true needs further study. Also to what extent can surfactants be developed that minimize or eliminate the need for cosolvents in applications involving crude oils?

Obtaining answers to these and related questions should be one of the principal objectives of research in surfactant flooding technology.

D. Miscible Gas Processes

1. Background. Miscible gas recovery processes offer the greatest potential for near-term enhanced recovery of light oil, with reasonable probability of significant production during the 1985-1990 period. A number of miscible gas projects are currently under way in the United States. Currently, the total production from all projects is about 50,000 bbl/day. The number of successful projects is expected to continue to increase, and miscible gas flooding can make a significant contribution (several billion barrels) to the total volume of oil over that recovered only by conventional processes.

Both hydrocarbon and nonhydrocarbon gases can be used miscibly to displace reservoir crude; however, the majority of recent field projects have utilized nonhydrocarbon gases such as carbon dioxide (CO_2) and nitrogen. Either of these gases can become a good miscible solvent if the reservoir has the right combination of crude composition, reservoir temperature, and pressure.

Neither CO_2 nor nitrogen is miscible with reservoir crude initially, but it generates a miscible solvent after injection into the reservoir. For example, when CO_2 is injected, it is "enriched" by extracting lower-molecular-weight components from the crude near the point of injection, leaving some "denuded" crude behind. The enriched CO_2 can be a very effective miscible solvent, capable of flushing the remaining oil from contacted portions of the rock. Nitrogen behaves similarly but normally requires considerably higher operating pressures to become miscible with the crude.

Additional research is needed, however, since the viscosity of an enriched CO_2 or nitrogen solvent bank is invariably much less than that of the crude oil. Consequently, the low-viscosity solvent bank tends to channel or finger through the formation, flushing only a limited fraction of the reservoir. In general, reservoir heterogeneity, gravity segregation, and viscous fingering in horizontal or low-dip reservoirs will all be serious problems and lead to low sweep-efficiencies in miscible gas floods. In steeply dipping reservoirs of high permeability, gravity segregation can prevent viscous fingering and provide much higher efficiencies of recovery. However, the number of reservoirs in the United States that satisfy the geological and fluid characteristics needed for gravity controlled floods is limited. Hence, other methods for controlling the adverse effects of viscous fingering are needed.

The method in most frequent use for reducing viscous fingering in nongravity-controlled floods is alternate injection of water and CO_2. This method, known as WAG or Water Alternating Gas injection, increases the fraction of the reservoir pore volume that can be contacted by the miscible gas; significant portions of most reservoirs will still remain uncontacted. Several patents have been issued for additives (primarily surfactants) that improve flood performance in laboratory tests, but their use in the field is likely to remain uneconomic unless adverse effects such as adsorption can be reduced significantly by future research. The development of new methods for improving mobility control and increasing the fraction of the reservoir contacted by miscible gas processes will be difficult but has high potential.

E. Thermal Processes

Of the various processes for enhancing oil recovery, thermal methods were the first to achieve significant commercial production rates. The two thermal recovery techniques that have proven technically and economically feasible have been steam injection and in situ combustion.

Steam injection processes for enhanced oil recovery usually occur in two stages: steam stimulation and steam drive. Steam stimulation is also known as "push-pull," "huff-and-puff," and "steam soaking." Each steam stimulation cycle consists of a period of steam injection to heat the oil and reservoir rock surrounding the injection well, a short "soak" period to permit the heat to distribute, and a production period. After stimulation, production rates rise rapidly to a peak and then decline as the heated oil is produced. With succeeding stimulation cycles, the production response declines until a point is reached at which it is more profitable to convert to steam drive.

In steam drive, or steam flood, steam is injected continuously at the injection wells to drive the oil through the reservoir to the production wells.

Oil production by steam stimulation has remained relatively constant at 130,000 to 140,000 barrels (20,000 to 22,000 cubic meters) per day over the past ten years. If production rates are adjusted to account for the fuel consumed in steam production, these rates decrease by about 18 percent. Production rates from steam flooding have increased from slightly over 10,000 barrels per day in 1978 to near 150,000 barrels (24,000 cubic meters) per day in 1977. The fuel adjustment for steam flooding, currently about 40 percent, is considerably greater than for steam stimulation and can be expected to increase as the reservoirs are gradually depleted.

The amount of oil produced by in situ combustion has been averaging approximately 10,000 barrels per day over the past few years. Recovery rates from combustion should increase in the future, but these increases are anticipated to be small relative to those realized from steam processes.

National Petroleum Council estimates for incremental oil recovery by thermal methods range from about 2 billion to 7.5 billion barrels (0.32 billion to 1.2 billion cubic meters).

Development of chemical additives to increase efficiency and reduce fuel requirements could extend the applicability of steam drive sweep and increase the ultimate oil recovery of thermal methods. Additives must be thermally stable at temperatures in excess of 175°C for long periods of time (5 to 10 years). This area has high potential for the development of new chemicals and of concepts for their effective use. Both avenues of research should be explored vigorously.

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6. RECOVERY OF METHANE FROM GEOPRESSURED RESERVOIRS

I. INTRODUCTION

The search for alternative sources of energy in the Gulf Coast region has focused primarily on potential thermal and methane resources contained within deep hydropressured and geopressured sediments. Initially, resource assessment studies were concentrated on geopressured sandstone reservoirs with fluid temperatures in excess of 150°C because these temperatures are requisite for electric power generation based on present technology. As the geothermal program matured and as natural gas prices increased dramatically, interest has shifted from thermal energy to the chemical energy represented by the methane dissolved in the brines.

The methane entrained in geopressured aquifers is a vast, widely dispersed resource of undefined magnitude. Estimates of the total amount of energy that can be extracted from geopressured reservoirs have dropped significantly from those made several years ago (see Table 1). The lower estimates are principally the result of better geological data. The number of geopressured reservoirs with favorable characteristics is now recognized as much smaller than was assumed earlier. A recent (June 1980) study by the National Petroleum Council estimates that 0.6 tcf (trillion cubic feet) of gas should be economically recoverable by the year 2000 at well-head prices less than or equal to $9 per kcf (thousand cubic feet) in 1978 dollars. (The study indicates that the volume of gas reserves should increase gradually above a threshold well-head price of $4/kcf to the above estimate at $9/kcf.)

Perhaps the most critical factor affecting predictions of the size of this resource is the current lack of knowledge concerning the salinity distribution of geopressured formation waters. Knowing the subsurface distribution of saline waters is important because (1) methane solubility is primarily controlled by salinity, temperature, and pressure, (2) the degree of corrosion and scaling of surface equipment depends on concentrations and chemical compositions of waters produced, and (3) the chemical composition of these waters and their compatibility with the water contained in shallower formations may control the long-term disposal of spent geothermal fluids.

TABLE 1. Estimated Gas Reserves in Geopressured Aquifers

Source	Date	In Place tcf*	Recoverable tcf*
USGS	1875 (onshore)	23,700	113 to 763
Jones	1976	50,000 to 100,000	258.2 to 1,146.0
ITISE	1976	3,000	28
LSU	1977	50,000 (La. only)	20
Lewin & Assoc.	-	-	1 to 42
DOE	1980	-	10 to 1,500
Univ. of Texas	1980	325	10 to 16
NPC	1980		0.6**

* Trillion (10^{12}) standard cubic feet.

**Estimated recovery at well-head prices of $9 per kcf or less in 1978 dollars. Based on Consumer Price Index data, this would correspond to a well-head price of about $11.35 per kcf in 1980 dollars.

Numerous physical and chemical mechanisms have been suggested to explain the wide range of subsurface salinities and their systematic and random changes observed in deeper parts of sedimentary basins. Ionic concentrations greater than those of seawater, commonly found at depth, are generally attributed to sediment compaction and dewatering of thick shale interlayers that act as semipermeable membranes. This process, termed ionic filtration (salt sieving, reverse osmosis), selectively allows the migration of water molecules through the sediment while movement of ions is retarded. Attendant transformation of expandable clay minerals to nonexpandable forms at temperatures above 90-100°C causes the release of water from interlayer positions. The low ionic concentration of this structured water would contribute to the dilution of shale pore water. The dynamic interaction of geopressures and osmotic pressures may explain the salinity contrasts found in adjacent sandstones and shales; however, several researchers contend that subsurface pressure gradients are inadequate to accomplish hyperfiltration in the face of osmotic pressures.

High-salinity brines in deep aquifers may also be explained by dissolution and ionic diffusion from nearby salt deposits, but proximity to salt is not requisite for high salinities. Other explanations for abnormal concentrations, such as evaporation or gravity segregation, have generally been dismissed because of quantitative considerations.

In Gulf Coast sediments below the top of the geopressured zones, where undercompacted shales exhibit higher porosities, reversals in trends toward lower salinities have been widely reported. Recent DOE-sponsored analyses of water produced from several geopressured reservoirs have measured a wide range of salinities ranging from less than 15,000 to over 200,000 ppm. These data suggest that current models that predict low salinities are not universally valid and that more comprehensive studies of the physical and chemical mechanisms are needed to explain the observed results.

II. CONCLUSIONS AND RECOMMENDATIONS

Many geopressured reservoirs along the Gulf Coast contain brines saturated with methane at reservoir pressures of 8,000 psi or more and temperatures in excess of 120°C. Although the ultimate potential of these reservoirs as a source of methane is not known, a recent study estimated that 0.6 tcf of gas should be recoverable at a cost of less than or about $9/kcf.

Since the amount of gas dissolved in brine depends on the composition and total salinity of the brine, analyses of a number of geopressured brines have been made. These analyses suggest that current simplified geochemical models of salinity are inadequate and more comprehensive and fundamental studies are needed of the physical and chemical mechanisms affecting the overall brine salinity and brine composition in different geopressured formations. Numerous laboratory measurements of methane solubility in brines as a function of temperature, pressure, and brine composition have been completed or are currently scheduled. A number of additional field tests in several geopressured reservoirs along the Gulf Coast will be required to resolve the overall potential of this source of gas. Comparisons of these experimental data with current theories of the solubility of methane, CO_2, and other gases in brines suggest that the theories are qualitatively correct. Several semiempirical equations have been developed to predict methane solubility at these high pressures and temperatures encountered in many geopressured formations; however, a sounder technical basis is needed for these predictions.

Other areas for chemical research are (1) the traditional problems associated with corrosion and scale formation accompanying the production of large volumes of high-temperature brine and (2) the solubility of gases in brines at high temperatures and pressures.

SECTION III: Alternative Energy Resources

7. SOLAR ENERGY AND BIOMASS

I. INTRODUCTION

Interest and research in the utilization of solar energy for the production of electricity and chemical fuels, and for heating and cooling, have expanded in recent years. The direct conversion of radiant energy to electricity is based on solid-state or liquid-junction photovoltaic cells utilizing semiconductor materials. Absorption of light at the interface between semiconductors (e.g., the junction between p- and n-type silicon or the junction between n-CdS and p-Cu_2S), at the semiconductor/metal interface (Schottky barrier) or at the semiconductor/liquid interface (in photoelectrochemical cells) results in the formation and separation of an electron-hole pair, accompanied by an electric current in an external circuit. The most highly developed of such devices, the Si photovoltaic cell, has already found widespread application and is undergoing considerable development. Photovoltaic cells can also be used to produce chemicals (e.g., H_2, halogens) either by external electrolysis or more directly in photoelectrochemical cells.

Solar energy can also be utilized for water and space heating. Such applications require the construction of collectors for conversion of the solar energy to heat, and means for storage of this heat. Storage systems generally involve inexpensive materials with rather low heat capacities (water, rocks), although chemical systems that allow heat storage by chemical bond formation or through phase changes have also been suggested. Solar energy has been suggested also for air conditioning and cooling purposes, for example, through the use of solar-driven heat pumps or metal hydride or zeolite materials. Fundamental chemical studies that bear on these applications are discussed below. Other less direct applications of solar energy, such as through wind and ocean thermal energy systems, are not considered here.

Because terrestrial solar energy is fairly diffuse (the average insolation over 24 hours is about 230 W/m^2 in the sunbelt), efficient and inexpensive collector materials are needed. Because it is intermittent, some provision for energy storage is usually desirable. Practical solar devices need also to be fairly maintenance-free and have long, useful operating lives (at least 10-20 years). Moreover, while the total annual solar flux is high, appreciable areas of land would be needed if solar energy were to meet a significant fraction of our energy needs. At conversion efficiency of 15 percent, about 0.4 percent of the U.S. land area would be required to supply half of our total energy requirements (based on usage in 1970). While a number of solar photovoltaic and thermal systems are already available, they do not meet the desired cost, efficiency, storage, and lifetime requirements, and fundamental research in a number of areas of chemistry is needed to overcome some of the critical problems. Indeed, new concepts and materials emerging from basic chemical research could provide "breakthroughs" in some areas (such as the utilization of solar energy for production of fuels), which could be as important to solar-energy utilization as the discovery of the transistor was to the development of computers. Research in this area, for the most part, pertains to long-term applications and diffuse economic returns. Therefore, chemical research on solar energy is unlikely to receive substantial support from private investment regardless of how large its public benefits may eventually be. This is an example of the kind of long-range fundamental research that will only be carried out on an extensive scale if it is supported by DOE and other government agencies.

The general areas of basic chemical research important with respect to solar energy are classified and described below in the following categories: solid-state chemistry; surface chemistry, photoelectrochemistry; photochemistry in homogeneous solution; membrane-, vesicle-, and micelle-based systems; energy transfer; and photosynthesis. Specific recommendations on research in these areas relevant to solar energy are given below. Research specifically in biomass energy is also discussed briefly below and discussed in detail in Section III.

II. RECOMMENDATIONS

Research in the following areas is recommended:

- Studies of new and established semiconductor materials, their properties, and methods of preparation.
- Experimental and theoretical investigations of semiconductor surfaces, surface states, and techniques of surface treatment and modification.
- Design of photocatalytic and photosynthetic systems (e.g., powders, micelles, vesicles, membranes) for the efficient decomposition of water and production of useful chemicals.
- Fundamental studies (experimental and theoretical) of the semiconductor-liquid junction and the factors affecting the energetics at the interface and the kinetics of surface reactions.
- Investigations of factors affecting energy transfer in thin films and other arrays, and the design and behavior of sensitizer molecules in energy and electron transfer reactions.

III. DISCUSSION

A. Solid-State Chemistry

The major problems are in semiconductor development for solar applications. Chemistry has a key role in the preparation of adequately pure semiconductors at an acceptable cost. It is also important in assuring adequate reliability and life of photovoltaic systems. Problems in this area will be delineated briefly. A number of other solid-state problem areas in solar conversion technology will also be mentioned.

1. New Materials. Advances during the last decade in the conversion of solar energy directly into electricity have been phenomenal, but no commercially exploitable large-scale installation is in operation. Attempts to lower the cost of silicon production and increase the efficiency of the photovoltaic cell have been successful and further near-term improvements seem probable, but the costs per unit of peak power and per unit of energy are still high. The replacement of single crystals by polycrystalline silicon, thin-film layers, and amorphous SiH_x films is one of the promising developments in which solid-state chemical research plays a large role. This research has produced contact materials that are transparent and conducting, as well as metallic compounds with large electronegativities. Their incorporation in the design of photovoltaic cells has boosted the efficiency, and other new materials may provide further improvements.

New semiconductors and new materials, both inorganic and organic, are needed for solar applications. Such materials as metal phthalocyanines and porphyrins, organic metallic conductors, conducting polymers, and merocyanine dyes have attracted recent interest for photovoltaic applications. In general, the efficiencies have been low and details of the charge separation processes, the effects of doping, and the conduction mechanisms have been lacking. Other than the ordinary considerations of cost and availability of materials, a number of fundamental problems are common to the field. These include: dopability (whether the material can be made n- and p-type), minority carrier lifetime, stability, grain boundary problems, availability of suitable metallizations, usable substrates, and processes for thin-film applications. Many of these problems are being solved only empirically, and the principles are not understood. Among more specific problem areas are the following.

Raw materials for semiconductors: Methods for producing and analyzing the reactants that form semiconductors (i.e., $SiCl_4$, SiF_4, $GaCl_3$, AsH_3, alkyl compounds of metals, etc.) are of concern.

Materials for reactors: The definition and development of container materials in which the semiconductor can be synthesized at high temperatures, and which do not react with nor introduce traps into semiconductors, is critical.

Substrates: The identification of new, inexpensive, conductive substrates that do not react with the semiconductors at high temperatures and do not introduce traps is essential. Problems to be evaluated include chemical compatibility and bondability at the semiconductor-substrate interface, lattice match, coefficient of expansion, and electrical properties.

Concentrators and collectors: Rheological, structural, and stability studies of plastics for the fabrication of Fresnel lenses, and the chemical causes for and the elimination of changes in the reflectance of metals, should be emphasized. All the reflecting surfaces now available undergo some degradation.

2. Polycrystalline and Amorphous Semiconductors. For both the well-established semiconductors (Si, GaAs, CdS) and the emerging semiconductors (CdTe, InP, $MoSe_2$, etc.), it is clear that solar converters will be viable only if the semiconductors are employed as thin films. Fundamentally, it must be established whether such films are best deposited in polycrystalline or amorphous form.

Chemical deposition methods: Reactions in which thin-film or bulk semiconductor materials are deposited from the vapor or from a liquid are of interest. Studies of reaction rates, phase diagrams, and equilibria are also important. Detailed studies of the chemistry and thermodynamics of nucleation on substrates, the chemical interaction of intermediate species on the substrate during growth, the processes of evaporation and condensation, and the chemisty of reagent streams [gas (chemical vapor deposition) or liquid (liquid phase epitaxy)] are needed before the growth of quality semiconductor materials can be routine and reproducible.

Film properties and characterization: Is the defect structure in amorphous materials such that they have inherently short minority carrier lifetimes? Is there reason to believe they will have stability problems? The bulk lifetime in the grains of many polycrystalline semiconductors is now too short. The types of defects and impurities responsible for these effects need to be understood in a number of diverse materials.

3. Material Stability. The chemical stability of homojunctions, heterojunctions, and metallizations under long-term solar irradiation needs study. Investigation is needed into the thermodynamics and kinetics of the solid-state degradation processes. These problems can be large in various heterojunctions such as CdS/Cu_2S and are suspected in some homojunctions as well. Some forms of various semiconductors, such as amorphous thin films, may be intrinsically unstable with respect to crystallization, etc.

Corrosion: Identification and understanding of corrosion processes in photovoltaic cells are needed for the design of cells that are economically sound. Electrochemical corrosion of contact metals and environmental degradation of sealants are particularly relevant.

Contacts: Obtaining optimum contacts is a major problem in solar materials technology. At present, contacts are an art rather than a science. A fundamental understanding of what types of contacts will be ohmic on various n- and p-type semiconductors is vital. Simple electron affinity arguments are not sufficient. An understanding of the chemistry of the semiconductor-contact interface is necessary to improve the ease of deposition, adherence, and stability of the contacts.

Encapsulants: Polymeric encapsulants are a critical yet neglected part of photovoltaics. The rate of transport of potentially corrosive atmospheric components through them, their stability to and protection against effects of light and the environment, the understanding and prevention of adhesion of dust and grime to their surface, all require study.

B. Surface Chemistry

Surfaces and interfaces are central to many aspects of solar-energy research because it is across these interfaces that chemistry, including electron transport, is mediated. Basic research is sorely needed in several areas.

1. Characterization of Surfaces. One of the underlying reasons for the renewal of interest in surface chemistry is the rapid development of sensitive techniques for surface analysis (e.g., all the electron spectroscopies). Among subareas where quality research is needed are the following:

- Development of site-sensitive, atom-specific probes of surface structure (for example, electron- and photon-stimulated desorption from metal oxide semiconductor materials).
- Development of new *in situ* spectroscopies (for example, surface enhanced and resonance Raman spectroscopy and surface extended x-ray fine-structure spectroscopy).
- Quantitative analysis of surfaces (this is an extremely complicated problem but a most important one).

2. Surface Modification. This area of research requires an intuitive approach guided by known principles of synthesis, molecular structure, and stability. The goals are to alter surface properties to achieve some desired end such as protection, electronic tuning, and optical tuning. Among major subareas are:

- Studies of overlayer bonding by means of electron spectroscopy.
- Development of synthetic pathways to build desired functionality and stability at a surface.
- Studies of optical and electronic coupling at organic dye-semiconductor interfaces.

3. Etching and Surface Treatments. Most of the materials involved in solid-state systems need to be etched at one time or another during fabrication. A better model of the chemical processes involved in etching is needed, as well as a program to develop the systematics for designing specific etches as a function of rate, sample orientation, and surface condition.

Chemical methods for preparation of perfectly transparent and perfectly absorbing surfaces: Production of surface hillocks of sizes smaller than the incident wavelengths make the surface of a semiconductor nonreflective. Similarly structured glass or plastic surfaces can make these "invisible." Chemical control of the surface topography of glasses, plastics, metals, and semiconductors will be important to either thermal or to photovoltaic conversion.

4. Nature of Surface States and Grain Boundaries. In any surface/interface problem involving chemical reactivity, optical activity, or charge transfer, the role of states localized at the surface must be established. The goal is to understand the underlying reasons for their occurrence and to manipulate their properties for various ends. For example, a number of thin polycrystalline semiconductor films about 10-100 μm thick with grain sizes of 0.1-20 μm have demonstrated considerable potential as solar converters in solid-state and in photoelectrochemical devices. To become economic, the substantial degrading effects of the grain boundaries on these devices must be overcome. The following topics need study:

- The role of surface structure and stoichiometry on the existence and properties of surface states.
- The role of adsorbates in altering surface states. Bulk defect states and surface states may be amenable to chemical passivation yielding substantially improved device efficiencies. Understanding the precise chemical nature of these states will require extensive study and theoretical developments.
- The role of surface states in photoexcitation, photoelectrochemistry, and photocatalysis.

The chemistry and physics of the grain boundaries in a wide range of semiconductors: silicon, the most studied material, is still only partially understood. Considerable effort needs to be directed toward developing passivating techniques for the grain boundaries in materials other than silicon.

5. Gas-Solid Photocatalytic Reactions. The use of photons to promote reactions at gas-solid interfaces is well known but is limited to a few reactions over a few solids. These processes are usually described only phenomenologically, and much research is needed to understand the molecular and charge dynamics. Among the most interesting topics are:

- Promotion of thermodynamically uphill reactions such as water decomposition and conversion of carbon (coal) to fuel gas.
- Chemisorption, stability, and desorption studies involving materials with known photoactivity.
- Design of new photocatalytic materials with a good response to the solar spectrum, utilizing known catalytic techniques (e.g., support-metal coupling).

C. Photoelectrochemistry

Solar irradiation of semiconductors in liquid electrolyte solutions currently represents the most efficient chemical approach to electricity and/or fuel generation from sunlight. While no practical technology yet exists, laboratory devices based on semiconductor/liquid junctions have given 12 percent solar conversion efficiency for electricity generation or 1 percent for direct generation of hydrogen and oxygen from water. As for all solar conversion schemes, chemical systems must be efficient, reliable, cost competitive, and safe. In order to achieve success, devices must have good solar response, output voltage, and current, and must be durable. Basic research to meet these criteria is needed in the following areas:

1. Electrocatalysis. Efficiency for H_2, O_2 generation from H_2O is low and could be significantly improved if the kinetics for the process could be improved. Electron transfer catalysts for H_2O H_2 and H_2O O_2 should be studied.

2. Synthesis of Large-Area Electrode Materials. The highest efficiency for semiconductor/liquid-junction devices for generation of electricity is obtained with single-crystal electrode materials. However, relatively good efficiency for polycrystalline electrode materials has been obtained. An effort directed toward synthesis of large-area (thin-film, polycrystalline, amorphous) electrode materials is needed to meet practical-scale technology.

3. New Redox Reactions. Most efforts in photoelectrochemical fuel production have focused on splitting water, with some emphasis on HX (X = I, Br). Intriguing leads for converting N_2 to NH_3 or CO_2 to CH_3OH by photoelectrochemical techniques exist. A program is necessary to elaborate the possible fuel-forming reactions that can be driven.

4. Surface Modification. Photoelectrochemistry is an interface science; significant improvement in efficiency has been achieved by surface modification of the semiconductor photoelectrode. Such modification includes etching, chemisorption of metal ions, deposition of metals, and covalent attachment of molecular redox reagents. Design and study of photosensitive interfaces is very likely a key to ultimately achieving a practical device.

5. Semiconducting Powders. Irradiation of semiconducting powders suspended in electrolyte solutions results in a number of reactions of possible significance in solar fuel production. Such reactions include generation of H_2 from H_2O and of CH_3OH from CO_2 and H_2O. These promising systems and exploratory studies of other systems should be pursued.

6. Semiconductor/Liquid Interfaces. Characterizing the interface by physical and theoretical techniques is essential to estab-

lishing factors limiting efficiency and durability. New, in situ surface probes are needed, and special emphasis should be placed on characterizing surface states believed to be important in charge-transfer kinetics and interface energetics. For example, surface states have been implicated recently in a number of instances where output photovoltages could not be understood within the framework of the prevailing interface models.

7. New Redox Systems. Electricity-generating semiconductor/liquid junction devices employ redox active materials. The most efficient cells use air-sensitive, toxic, light-absorbing materials as redox reagents. Exploration of new couples should be undertaken to enlarge the number of options. Special emphasis is needed on systems stable toward air and moisture in order to realize an advantage compared to solid-state photovoltaic cells for solar electricity.

8. Transport. Basic transport problems require solution through understanding and analysis of scaled-up photoelectrochemical cells. Flow, thermal conduction, and light absorption by the oxidized (or reduced) redox couple will have to be modeled, and appropriate cell structures will have to be conceived and mathematically analyzed.

D. Photochemistry in Homogeneous Media

Photochemical reactions in homogeneous solutions can be used to produce reactive chemical species or fuels and to store thermal energy. For example, photogalvanic cells based on the reaction of an excited thionine molecule with ferrous ion have been investigated. Similarly, homogeneous reactions for production of hydrogen have been proposed. Generally, the efficiency of such processes has been rather low. The efficient conversion of solar energy into valuable chemicals or fuels requires the diversion of a large fraction of the electronically excited molecules into "useful reactions." These reactions must be driven in competition with rapid physical deactivation processes and fast chemical back-reactions.

1. Electron Transfer Reactions. Further studies are needed of the factors determining electron transfer rates of ground- and excited-state species, particularly in the extreme exothermic and endothermic energy regions. Much more information is required about the nature of the intermediates in complex, light-induced electron-transfer reactions: a very important research area is the chemistry of low oxidation states of metal complexes in aqueous solution. Such oxidation states are important intermediates in the photoinduced reduction of water to hydrogen, and they could function as homogeneous catalysts in a variety of new energy-intensive reactions.

2. Homogeneous and Heterogeneous Catalysis of Redox Process Homogeneous and heterogeneous catalysts can dramatically change the course of the reactions of the primary products of excited-state reactions. The use of heterogeneous catalysts to promote desired reactions

(and to avoid undesirable ones) requires improved methods for the preparation and stabilization of finely dispersed metal and semiconductor powders. An important new area where more work is needed is the *in situ* generation of colloidal catalysts. The various preparations need to be characterized by a variety of physical (light-scattering) and chemical techniques, and standard conditions for the assessment of the efficiency of different catalysts need to be defined. Catalysts need to be developed with highly specific properties, for example, the ability to catalyze the formation of hydrogen but not of oxygen (and vice versa). The aqueous chemistry of hydrides and of coordinatively unsaturated complexes needs much further study. Detailed theoretical study is required on the extent to which the dispersed systems can be treated as microcells.

3. *Chemical Storage of Thermal Energy.* The storage of thermal energy in chemical systems is another area where more research is needed. Chemical systems suitable include phase transitions, isomerizations, and chemical equilibria. Information is needed about the thermodynamics of promising changes and about the thermal and photochemical stability of the reactants and products. Methods should be sought for controlling the rates of back-reactions and side-reactions. Additional work on the sensitization of organometallic systems is needed. The fundamental issue to be settled is whether or not adequate barriers can be achieved against reversal of the photochemical reactions, simultaneously with good absorption (in the region λ = 4000-9000 Å). Conceivably, there are fundamental kinetic reasons why such storage will not be possible.

E. Photochemistry in Organized Media Including Micelles, Vesicles, Membranes, Polymers, and Other Interfacial Systems

Recent studies of photoreactions--particularly light-driven electron transfer processes--in organized media or interfacial systems have indicated that incorporation of excited substrate or reactant or both in these media can modify rates of various processes as well as overall net chemical reactivity. In several cases, such photochemical reactivity has been used as a probe to provide detailed structural information on the specific microenvironment of the organized media or a particular "pseudophase" therein. By far the most extensively investigated area has been the modification of rates for light-driven electron transfer processes and subsequent dark reactions in micellar media. The results obtained thus far suggest that considerable control of these processes can be effected so that the lifetime of reactive reagents generated by excited-state quenching processes can be either greatly increased or sharply reduced. One of the major interests in future will be to adapt this "control," which can be obtained by the use of micelles and other organized media, to develop useful net chemical conversion of solar energy. A common property of these systems is the presence of a surface active agent. Self-assembly leads to the formation of aggregates distinguished by an apolar region and a charged lipid/water interface. The latter affords a microscopic electrostatic barrier, which can be exploited to achieve light-induced charge separation and storage effects.

1. Artificial Membranes. Artificial membranes, such as black lipid bilayer membranes (BLM), can be extended over an orifice several millimeters in diameter, separating two aqueous compartments. These membranes have served in the past as reference systems for more complex biological aggregates. Their application to solar-energy conversion is hampered by the fact that BLM are unstable and light absorption by incorporated dyes is small. With regard to stability, the development of two-dimensional polymer networks appears promising.

2. Micelles. These spherical assemblies form spontaneously in aqueous solutions of surfactants and are thermodynamically stable. Light-induced charge separation has been achieved in several important redox reactions. Crucial for the eventual application of micelles will be their compatibility with catalytic entities making use of the energy stored in the redox products. The design of appropriate colloidal catalysts will be a key to the exploitation of the potential offered by these systems (see Section D.2). Investigations into the factors that control the dynamic nature, size, and stability of micelles will be required for the development of practical systems.

3. Vesicles. A vesicle may be regarded as a closed BLM arranged in an eggshell fashion separating an inner water pool from the aqueous bulk. Studies of light-energy conversion in such systems have started only with the advent of synthetic surfactants as vesicle-forming agents. Much investigation is needed into the development of larger systems such as liposomes or vesicles based on charged polymers (both soluble and insoluble), which incorporate many of the features of micelles including a controllable pseudophase with greater stability and controllable mobility. Basically, light-driven electron transfer reactions generate strong one-electron oxidants and reductants, which must be reacted subsequently to derive net useful chemistry. Possible means of accomplishing this include redox processes at an electrode whereby generation of electricity and production of a fuel or useful reagent can be coupled with recyclying of the one-electron reagent. An alternative is the employment of a catalyst that couples redox processes of the one-electron reagents with poly-electron conversions of a secondary substrate (e.g., oxidation or reduction of water mediated by catalysts such as colloidal platinum or ruthenium oxide). Currently, there is a major gap in knowledge of how reactions occurring in organized media can be interfaced with electrochemical or catalytic processes, and major efforts in this area are clearly needed. While investigations previously mentioned have shown the potential for modifying lifetimes of reactive intermediates, much more work is needed to develop organized media that will accomplish net separation of oxidizing and reducing power. Future investigations should focus on immobilized substrate systems (reactants) coupled with mobile reactants (substrates); organized media could be developed to accomplish this by providing either an immobile support or a selective barrier or membrane.

F. Energy Transfer

In many solar-energy applications it will obviously be advantageous to have light-absorbing moieties (the chromophore) bound to an insoluble substrate such that (1) photochemical products can be easily separated for utilization or (2) the excited chromophore is in proximity to a suitable electrode surface with concomitant photoionization. The absence of physical diffusion for a bound chromophore in the excited state will diminish the efficiency of subsequent photochemical processes that require "collision" of the chromophore with some other molecule or surface. This can be offset by energy migration among an array of chromophores, providing a kind of "antenna effect" in which light absorbed anywhere on the array has an excellent chance of finding a reactive site.

In artificial or biological photosynthesis, light "harvesting" by antenna molecules and transfer of energy to the center of the chemical action are the core of two processes involved:

Biological photosynthesis (A): light → antenna molecules
reaction center → chemistry.
Artificial photosynthesis (B): light → antenna molecules
photovoltaic devices → electric energy.

In (A), the molecules involved are chlorophylls, and in (B), the molecules involved are dyes or ions.

Energy transfer takes place in essentially all devices that utilize photon absorption or emission. The transfer of energy can be accomplished either by exploiting processes "inside" molecules (intramolecular) and/or between molecules (intermolecular) or ions. Hence, fundamental understanding of the photophysical and photochemical channels responsible for intramolecular and intermolecular energy transfer is essential. While the general subject of electronic energy transfer has been extensively studied in van der Waals solids and between isolated molecules, arrays of the type likely to be relevent to solar-energy conversion have not been studied extensively, and as a consequence one is not in a position to "design" arrays to perform a desired energy-collection task. The following areas are of importance in understanding energy transfer processes and designing antenna arrays:

1. Rates of Energy Transfer. Techniques and accurate methods for measuring the rates in vivo and in model systems are required. Research in this area involves the use of laser technology in connection with state-of-the-art technology in electronics and optics; rather sophisticated instrumentation may be needed. Fundamental questions to be answered are:

What is the physical nature of different arrays that may be lumped under the heading of "ultra-thin films"? Under what conditions will facile energy transfer be observed? What are the important properties of the chromophore molecules that determine the energy migration rate, for a given type of array? These are essentially experimental questions.

Can appropriate theoretical models be constructed that will unify the observations on various types of arrays? One theoretical difficulty is that most of the above systems are disordered, such that modeling may require computer simulations rather than closed, analytical solutions. Theory should be expected to play an active role in these problems, both as a guide to experiment and as an interpretation of experiment.

The effect of environment on energy transfer: the quenching of "useful" energy by chemical and physical means must be studied in order to design systems with optimum efficiencies. The studies may include photophysical measurements with spectroscopic probes.

Electron transfer versus energy transfer: the sorting out of electron and excitation transfer is mandatory before the overall mechanism can be understood. The rates, yields, and dynamics of electron transfer must therefore be studied.

2. New Designs of Collectors and Arrays. Considerable attention is being directed toward enhancing device efficiencies by embedding various adsorbers and luminescers in a number of solid matrices. The chemistry and photophysics of the chromophores in these devices need considerable fundamental study. The stability of the absorbing and luminescing species is a major problem. The chemical compatibility and stability of the matrix material must be evaluated. Basic research into the factors affecting the configuration of such assemblies include the following topics.

Collective effects and light harvesting: in many cases, energy transfer proceeds only if there is a collective network among the excited chromophores. Studies of these collective properties may require high-resolution spectroscopy and modern laser techniques. Theoretical modeling will also be of value.

Chromophores can be chemically bound to a surface, or physically adsorbed with sufficient binding energy to resist desorption by solvent, or by sublimation in gas-phase applications. As a special case of this array, polymers containing suitable chromophores can be bound to appropriate metal oxide surfaces. In the former case, energy transfer can occur between chromophores if their density is high enough. In the latter case, intramolecular and intermolecular energy transfer can occur. The orientation of chromophores with respect to each other is expected to be random.

Monolayer assemblies of the Langmuir-Blodgett type can be prepared in which interlayer and intralayer energy transfer can occur. Since these assemblies are normally constructed with "spacer" molecules (hexadecane or cadmium salts of long-chain fatty acids are typical), one expects the mutual orientation of the chromophores to be random, although in some cases ordering may be possible.

Suitably cross-linked polymers are useful substrates for polymer-bound catalysts because they admit solvent without being dissolved. Similarly, chromophores bound to cross-linked polymers can act as photosensitizers, and if the chromophores are present in sufficiently high density along the polymer chain, energy transfer could, in principle, enhance the overall efficiency.

Not all chromophores are equally suited for solar-energy applications. The most universal requirement is that a strong absorption in the visible to red region of the spectrum be present. Secondly, the excited chromophore must be capable of some photochemical process to capture the photon energy. Certain of the parameters that will govern the nature of the array and the energy transfer processes are molecule specific (e.g., molecular size, polarity, solvation, magnitude, and orientation of the transition dipole). Consequently, the physical arrays discussed above must be constructed from chromophores suitable for solar absorption if at all possible.

3. Application of Sensitizers to Photochemical Processes at Surfaces. Chromophores attached to surfaces can be employed to improve the efficiencies of photoprocesses at semiconductor surfaces, e.g., in gas-phase reactions (see Section B.5) or at electrodes (see Section C.4).

Photochemical reaction of bound chromophore with solution or gas phase molecules: in this case, intimate contact between the mobile phase and bound phase is required. Thus substrates with large surface areas, such as powders or cross-linked polymers, must be used. If the chromophore array is improperly designed, significant portions will be excluded from contact with the mobile phase, resulting in wasted light energy. Consequently, one can anticipate that the arrays will be topologically equivalent to disordered or ordered monolayers.

Sensitization of photoelectrode processes: an excited sensitizer molecule, to be effective, must approach an electrode to within an electron transfer distance, which will be on the order of a molecular collision distance. From this point of view a monolayer is ideal. However, the absorbance of a monolayer is very low, even for dye molecules, so a multilayer structure is preferred. As before there is likely to be an optimum "thickness" of this layer such that absorbance is maximized subject to the constraint of high probability of energy transfer to the electrode-chromophore layer interface.

G. Photosynthesis

Research on photosynthesis is an integral part of the DOE effort on solar-energy conversion and storage. This is of course entirely appropriate because photosynthesis is nature's way of solar-energy conversion and energy storage. The unraveling of the mechanisms of the natural processes will benefit the design of efficient synthetic devices for possible future use in solar-energy conversion. For example, one of the most important problems to be solved for artificial systems is how to prevent the so-called "back reaction" in electron transfer processes. When a molecule in a photoexcited state acts as an electron donor (or acceptor), the ion pair thus created contains chemical potential that can, in principle, function as a useful energy source. However, in many artificial systems, a large fraction if not all of this energy is wasted in the "back reaction" in which the electron transfer is reversed, creating heat and leaving the molecular system in its electronic ground state. Somehow, in the natural photosynthetic apparatus of bacteria and green plants this back-reaction is avoided and the chemical potential is put to use. Clearly, a detailed understanding on the molecular level of charge separation in natural systems would be of tremendous benefit.

There has been considerable progress in photosynthesis research over the past 10 to 15 years. Much of the work has been supported by DOE and its precursor agencies (ERDA, AEC). Modern spectroscopic tools, notably electron spin resonance and picosecond optical spectroscopy, have promoted at least a rudimentary understanding of the primary events in photosynthetic systems. Because photosynthesis in bacteria is less complicated than in plants, much of this understanding comes from the study of bacterial systems.

1. Summary of Photosynthesis. In both bacteria and green plants, the majority of the chlorophyll molecules function as light-harvesting pigments and constitute the so-called antenna. The excitation caused by an absorbed photon arrives through a series of Förster energy transfer steps at the so-called reaction center where the photochemistry takes place. In bacterial systems, it is possible to separate the reaction centers from the antenna, while in plants reaction centers so far have only been enriched. Bacteria reaction centers are made of a lipoprotein of 10^5 daltons containing four chlorophyll molecules and two pheophytins (chlorophyll without the magnesium atom). Two of the chlorophylls form a special pair $(BChl)_2$, which accepts the excitation from the antenna and functions as the primary electron donor. Within a few picoseconds, the excited state of the special pair donates an electron to an acceptor (A) which at present is thought to be a pheophytin molecule. Then, in nanoseconds, a second electron transfer takes place from the reduced pheophytin (A^-) to a quinone-iron center, which for historical reasons is called the primary acceptor. From there a series of additional electron transfers takes place too complicated to elaborate here. It suffices to say that a proton gradient is established across the membrane creating the driving force for ATP synthesis. In bacteria, the oxidized special pair is reduced by cytochrome. In green plants, the pair is reduced by a second photosystem, PS II, which is ultimately coupled to the oxidation of water. Manganese ions are thought to be involved in the water oxidation, although the proposed mechanisms are entirely speculative.

2. Antenna Systems. Much of the efficiency of the natural photosynthetic apparatus resides in a light-harvesting system, which collects and transfers the incident excitation to the reaction centers. Much more work is needed before a clear understanding of the energy transfer mechanism will emerge. Most of the possible approaches are listed in the section on Energy Transfer and need no further elaboration here.

3. Reaction Centers. Since reaction centers have never been crystallized, almost no structural information is available. Yet, if further progress is to be made, structural information is urgently needed. Crude estimates of distances separating the various acceptors

can be and have been obtained by magnetic resonance methods. Perhaps a major effort should be applied to obtaining crystalline reaction centers or subunits thereof. Another area meriting more attention is the mechanism of O_2 formation in green plants. This reaction is of direct importance for artificial solar-energy conversion. In general, the events in green plants are much less well understood than those in bacteria. A major effort should be directed to isolation of green-plant reaction centers. This calls for collaboration of biological chemists and protein chemists. Other important questions concern the role of carotenoids as protection agents.

4. Model Studies. Model compounds and systems have always played a role in the study of complicated biological processes, and photosynthesis is no exception. Work on positive and negative ions of chlorophylls provided the optical and magnetic resonance data necessary to identify these species *in vivo*. More recently, covalently linked dimers have been synthesized and assembled into larger systems that mimic some of the primary photosynthetic events. Some of the photophysics detected in bacterial and algal systems has never been duplicated in *in vitro*. Model work is essential for understanding these highly unusual phenomena. A strong effort should continue in this area. For the effort to be successful, it is essential that synthetic organic chemists be attracted to these problems.

H. Biomass Energy

Utilization of biomass as an energy source has a long-standing history and in future may supplement fossil fuels importantly. Basic research into increased use of biomass as an energy source is a multidisciplinary effort involving agriculture, biology, biochemistry, biophysics, chemistry, and chemical engineering. This brief section of the report in no way attempts to present an overview of the potential research opportunities in biomass production and utilization, but rather is restricted to certain aspects where basic chemical research may have an impact.

1. Biomass Production. Basic research in photosynthesis and plant growth bears on possible increase in the efficiency of plants as converters of photosynthetic materials into other products (e.g., cellulose, oils, organic carbon, and hydrogen). The research should address the reasons for the relatively low overall efficiency of photosynthesis and possible ways to improve it. Research in plant growth factors should continue to be vigorously pursued.

2. Conversion Technology. The chemistry involved in the combustion, gasification, and liquefaction of biomass should be investigated and also the secondary gas-phase chemistry. This research is closely related to that on combustion of fossil fuel, and each area should be cultivated with full knowledge of the other. The chemistry of lignocellulose (e.g., wood, grasses, and crop residues) is in need

of basic research to separate the components and convert them to useful products. Bioconversion of lignocellulose is a possibility.

3. The Production of Fuels by Biological Means. Methanol and ethanol are the liquid fuels most directly obtainable from biomass. The problem with ethanol obtained from fermentation is the energy required for separating it from water. Research on alternate concentration methods should receive high priority. Methods exist to convert alcohols to higher-grade fuels. Production of methanol from cellulose is possible but not currently economically feasible. Other conversion methods such as thermochemical gasification and thermochemical liquefication should continue to be investigated. Hydrogenation of cellulose to methane is possible in principle, but research is needed to develop a practical process. The direct production of hydrocarbons from plants such as euphorbias and asclepias may be feasible as a source of chemical materials and energy. Research should continue on chemical processing to extract the hydrocarbons after harvesting, as well as biological research on improving plant yield.

8. GEOTHERMAL ENERGY

I. INTRODUCTION

Our planet Earth is a gigantic heat sink, whose heat content dwarfs the energy requirements of mankind. This chapter reviews the magnitude of our geothermal energy resources, the extent to which they are currently being developed, the types of geothermal energy available for utilization, the problems standing in the way of fuller utilization, and the role of basic chemical research in overcoming some of these problems.

Combustible fuels associated with geothermal sources of energy, such as geopressurized methane, are covered in Chapter 6 of this report. The concern here is with enthalpic energy available from the surface and interior of the earth.

Several detailed studies of geothermal resources have been published during the past half dozen years. One of the most recent, "Geothermal Resources and Technology in the United States," Supporting Paper 4 for the Report of the Committee on Nuclear and Alternative Energy Systems (CONAES, National Academy of Sciences, 1979), is a critical re-evaluation of the conclusions reached in U.S. Geological Survey Circular 726, a comprehensive survey of U.S. geothermal resources published in 1975. In a later publication, U.S. Geological Survey Circular 790, "Assessment of Geothermal Resources of the United States, 1978," the Department of the Interior, in cooperation with the Department of Energy, refined, expanded, and updated the earlier publication, and, in general, substantiated the overall conclusions of Circular 726. The Geological Survey estimates are in reasonable agreement also with those published in 1979 by the Hot Dry Rock Assessment Panel convened by the Energy Research and Development Administration.

These and other government-sponsored studies, and numerous nongovernmental publications, contain such a wealth of detail concerning the magnitude of geothermal resources and the methods by which they are being, and might be, utilized that it is unnecessary to reiterate their content in depth. Instead, their general conclusions will be summarized to the extent necessary for the purposes of the present report.

II. CONCLUSIONS AND RECOMMENDATIONS

Geothermal energy represents a vast, virtually untapped source of energy that could be used directly for a variety of industrial, space-heating, and electrical purposes. In view of its great potential as an indigenous, abundant source, considerably more research should be funded in areas that would contribute to accelerating its development and widespread use. Among such areas involving basic chemical research are the following:

- New drilling materials, logging methods, systems for transmitting logged information, and other devices are needed, adapted to the high temperatures, high pressures, and hostile environments encountered in deep wells.
- Research should be encouraged on the hydrothermal behavior of mineral systems encountered at great depths, the phase changes that occur when brines of deep origin are brought to the surface and cooled, and the mechanisms and control of scaling and corrosion encountered in the handling of such brines.
- New systems will be needed for the control and utilization of the heat available from various geothermal sources, particularly those at greater depths.
- Theoretical and experimental research should be fostered on the impact of widespread tapping of geothermal energy on the environment, such as geologic stability, surface-level radiation, and chemical contamination of the atmosphere and of groundwaters.

III. DISCUSSION

A. Magnitude and Distribution of Geothermal Energy

The Earth, with a volume of 1.08 x 10^{12} km^3, a mass of 6 x 10^{24} kg, and a mean radius of 6371 km, comprises the following concentric layers:

A core of 3470 km radius, of which the central portion is probably solid metal as a result of the high pressure (3.7 x 10^6 atm at the center), and the outer portion (2170 km thick) is molten metal, mainly iron. The temperature of the central core is believed to be about 4000°C, and that at the core boundary about 3000°C.

A mantle about 2900 km thick (mainly siliceous rocky material), of which the inner portion 2000 km thick is homogeneous in composition and more deformable, and the outer 900 km is more rigid.

A crust, about 35-40 km deep below the continents, which cover 30 percent of the Earth's surface, and much thinner (about 5 km) below the oceans.

The lithosphere is the rigid outermost portion of the Earth, including the crust and the upper mantle, to a depth of about 50-100 km. It overlies the asthenosphere, or lower portion of the mantle, which is partially melted and plastic, although of very high viscosity (about

10^{20} poise). The lithosphere is believed to be divided into a number of plates (seven major and about a dozen minor) about 100 km in thickness, which move relative to each other at a rate of several centimeters per year over the underlying plastic asthenosphere. According to the concept of plate tectonics, the forces at plate boundaries cause instabilities that have several effects. They permit intrusion of higher-temperature, lower-density material from the mantle, cause stresses that may result in earthquakes, and, in subduction zones where interplate contact forces one plate to descend into the asthenosphere, cause the generation of magma (melted rock). Magma has a relatively low viscosity ($\sim10^3$ poise), and its ascent to or nearly to the surface, during millions of years, may induce volcanic eruptions, cause geysers, or create deposits of "hot rock" of high enthalpy.

The total heat content of the Earth, including core, mantle, and crust, relative to a cooled temperature of 50°C, is calculated to be about 1.5×10^{13} quads (1 quad = 10^{15} B.T.U. or 10^{18} joules), ignoring heat released by phase changes. The corresponding amount underlying land areas is 4.6×10^{12} quads, and that underlying the United States is 2.8×10^{11} quads. The bulk of this energy, of course, is inaccessible by any known means; the figures are cited merely to show the tiny fraction of the Earth's total heat content required by the energy needs of mankind--78 quads per year for the United States, about three times that amount for the whole world. To supply the world's energy needs, at present levels, totally from geothermal sources for 25 years would lower the Earth's temperature by one-millionth of a degree Celcius, if equilibration were maintained. Even this lowering would be lessened by heat liberated by radioactive decay within the Earth's crust, which provides part of the outflow of heat through the Earth's surface of about 800 quads per year.

The amount of more accessible geothermal energy is far smaller than the total heat content, but still large in terms of energy use. The heat available in the outermost 10 miles of the Earth's crust is estimated at 1.2×10^9 quads, about 2000 times the energy that would be released by combustion of the world's entire coal supply. The CONAES panel estimates that the total U.S. geothermal energy reserve with heat content above 80°C and recoverable at a depth of not over 6-7 km, is about 1.5×10^6 quads, excluding national park area. If restricted to heat practically producible and usable, the total is severely reduced to 22,675 quads. The 1978 and 1975 estimates of the U.S. Geological Survey (USGS) are larger than these but are based on somewhat different assumptions and classification. Since both estimates lead to the conclusion that usable geothermal energy resources are large in terms of needs--sufficient for hundreds of years--a detailed comparison of the two is unnecessary for the purposes of this general review.

B. Extent of Use of Geothermal Energy

In spite of the large amount of energy potentially recoverable from geothermal sources, and the long history of the use of such energy for generation of electricity (dating from an Italian generator started in

1913), development has been slow. Estimates of current U.S. capacity range from 0.03 to 0.08 quad, at most 1 percent of U.S. generating capacity or 0.1 percent of total U.S. energy requirements. Estimates during the early 1970's of the probable development of electrical generation in the United States from geothermal energy range from "insignificant as a factor in national power capacity (less than one percent of the total) through the year 2000" (U.S. Department of the Interior, 1972) to the more optimistic view that geothermal sources could produce almost 20 percent of the power needed in 1985 (Hickel Geothermal Resource Conference, 1972). The reasons for such wide divergence of opinion will be more readily apparent from a discussion of the manner in which applications of geothermal energy have developed.

C. Types of Geothermal Energy Available

The normal outward geothermal heat flux at the surface of the Earth averages 1.25 x 10^{-6} cal/s cm^2--far too dilute to be collected for useful purposes by known economically feasible methods, and, for the most part, too low in temperature to be used with high thermodynamic efficiency. (The solar-energy input to the Earth's surface is some 10^4-10^5 times as great, and still its direct thermal utilization is of limited usefulness.) However, the outflow of geothermal heat is not uniform over the Earth's surface, because of irregularities, faults, and discontinuities in the Earth's crust. As a result, there are regions where geothermal heat is accessible at higher than average flux and temperatures, and where historically the use of geothermal energy has developed. Such energy has been classified into six types:

1. Hot-Water Reservoirs. Water seeping through permeable rocks in the Earth's crust may contact high-temperature rocks at lower depths, which heat the water and cause it to rise convectively. If the heated water is trapped by formations that prevent it from reaching the surface, it may accumulate as a convectively circulating body, eventually reaching a thermal steady state in which heat loss to the surroundings is balanced by heat acquisition from hot rock. Such water is generally under pressure and may range in temperature from just above ambient surface temperatures to 350°C or higher. It becomes saturated with the minerals it contacts, the hotter bodies containing more dissolved mineral matter than the cooler. In the United States, the mineral content of such waters ranges from less than 0.1 percent to over 30 percent. Waters containing low concentrations of dissolved solids may be used directly for space-heating and other low-temperature uses, but the higher-temperature waters containing higher concentrations, while suitable for running electrical turbines, must be treated to remove solids in order to prevent scaling and corrosion.

Hot-water reservoirs may manifest their presence by seepage to the surface through porous rock or fissures, forming hot springs or geysers (mixtures of water and steam). The famous geysers of Yellowstone Park derive their geothermal heat from an underlying silicic magma chamber a few kilometers below the surface; this chamber has an estimated volume of 45,000 km^3 and a remaining heat content (despite a million or more years of cooling) of 67,000 quads. Intrusion of higher-temperature magmas from beneath this body could inject further large quantities of heat.

The CONAES report estimates that the total thermal energy potentially available from hot-water reservoirs is 6000 quads, excluding sources at less than 80°C, those in national parks, and those requiring drilling to depths greater than 3 km. Of this amount, about 10 percent has already been discovered.

2. Steam Reservoirs. If the pressure in a hot-water reservoir is insufficient to maintain the water substantially completely in the liquid state, a pocket of steam is formed, which may escape by natural fissures (forming a fumarole or geyser) or may be tapped by drilling. The steam thus obtained is reasonably pure, with carbon dioxide and hydrogen sulfide as the usual major impurities; the mineral content of the hot-water phase remains with the liquid as the steam boils off. Steam from such fields is characteristically delivered at temperatures of 230-250°C. The CONAES report estimates that only 45 quads of useful energy are potentially available from steam reservoirs in the United States, under the same limitations mentioned in connection with hot-water reservoirs. Such reservoirs are not common, but in the United States are the source of the world's largest geothermal electrical power-generation complex, at The Geysers, in California, which first began operation in 1960. Other dry-steam plants are in use in Italy and Japan.

Direct use of such steam, with the included carbon dioxide and hydrogen sulfide, requires the use of turbine blades made of corrosion-resistant alloys that have low stress characteristics, so that the turbines must be run at relatively low speeds and efficiencies. The current needed to make generator effluents environmentally acceptable could be met by purifying the steam upstream of the generator. This option, together with the development of higher-strength alloys, may lead to more efficient generators.

3. Geopressurized Brine Reservoirs. In some areas, such as the Gulf Coast in Louisiana and Texas, there are thick, deep beds of sandstone and shale with pores containing water entrapped by the chemical and physical changes occurring during geologic time--changes that have deposited and compacted additional sediment above the water-bearing strata. As a result, the water sustains pressures several thousand pounds per square inch above the hydrostatic pressures normal to these depths. Because such waters do not circulate much, their temperatures usually vary over a rather narrow range between 140°C and 79°C, with an occasional source above 180°C. As previously mentioned, such geopressurized waters are believed to be saturated or supersaturated with methane, which is liberated when the water is withdrawn. The potential of this geopressurized methane as a source of energy is discussed in Chapter 6.

Although geopressurized brine is at only moderate temperatures, the large volumes available provide a sizable total source of energy, estimated in the CONAES report at about 2400 quads producible from accessible onshore reservoirs to a depth of 7 km, at temperatures above 50°C. From this energy must be substracted the considerable amounts required to raise the brine, to remove from it undesirable contaminants, and to reinject it. Reliable data are needed on the net energy recoverable from such deep brines.

4. Normal-Gradient Heat. Between the surface of the Earth and the upper mantle, where temperatures may reach 1000°C, there is a temperature gradient averaging 30°C per kilometer. With such a gradient, rock at useful temperatures (80°C) is reached at a depth of 2.2 km. Rock at temperatures useful for generating electricity is found at a minimum of 4.5 km (150°C), and at even more effective temperatures (195°C) at a depth of 6 km, which has been assumed to be the maximum depth economic for drilling by current techniques. No demonstrated technology exists for the useful exploitation of this normal-gradient heat at present, but methods refined for the extraction of heat from higher-gradient sources (see below) are likely to prove adaptable.

The amount of enthalpic heat available in this form is quite large. The CONAES report estimates it to be about 12,500 quads of accessible and potentially producible energy in the United States at temperatures above 80°C, including over 3000 quads above 180°C. These figures were reached on the assumption that only 1 percent of the useful enthalpic heat eventually would be recovered.

Normal-gradient heat may have a particular appeal outside the United States, particularly in deprived countries. Like solar radiation, it is available everywhere in the world, in quantities likely to provide for much of the energy needs of each country from indigenous resources for many years to come.

5. Hot Dry Rock (HDR). A higher-than-normal temperature gradient occurs in some areas because of faults, irregularities in the Earth's crust, or volcanic action. Gradients of 40°C/km or more permit access to high-temperature rocks at shallow and economical well depths. Rock beds of this type, if water is absent, are classified as HDR. Generally, rocks so classified have temperatures above 150°C and are found at depths below 10 km.

The USGS has estimated that about 5 percent of the total U.S. land area overlies rock having thermal gradients exceeding 40°C/km, and one third of the land area overlies thermal gradients above average, in the range of 30-36°C/km. Estimates of the heat content of HDR in the continental United States (excluding Alaska), to a depth of 10 km and at temperatures of 150°C or higher, have ranged as high as 105,000 quads. The CONAES report limits the probable HDR potential to formations accessible and reached at depths below 6 km, assuming that only 1 percent of the available heat would be recovered usefully. Within these restrictions, the HDR thermal energy available is estimated at 1635 quads, including 525 at 80-180°C and 1110 above 180°C.

Indicative of the extreme deviations occasionally found from the usual gradient patterns is the discovery a dozen years ago of an HDR formation with a temperature gradient of 300°C/km underlying an area in Montana of about 4 km radius. HDR at 500-700°C lay less than 3 km below the surface, and useful temperatures could be found at 1 km or less. This formation was believed to be an igneous intrusion that had not yet fully cooled--a magma chamber that did not erupt to the surface and solidify.

The techniques being investigated for the utilization of hot dry rock involve access to the rock by one or more boreholes, injection of water, and use of the steam generated to run turbines directly for electricity or, by heat exchange, to vaporize a secondary fluid that in turn will run the turbine in a closed cycle. Detailed calculations of the efficiencies for a number of such secondary fluids predict attractively high optimum values within the geothermal fluid temperature range of 100-300°C.

A major problem in such systems is the development of sufficient hot rock surface at the bottom of the well to transfer heat to the injected water fast enough to sustain the required rate of vaporization. Various fracturing systems have been proposed, including nuclear explosions. Hydraulic fracturing appears to have been successful in a field experiment conducted by Los Alamos National Laboratory in New Mexico, in which energy was extracted at a rate of five thermal megawatts for 75 days. A 10-MWe HDR pilot plant is expected to begin operation in 1982, and a 50-MWe demonstration plant in 1986. The success of these may well determine how rapidly HDR generation systems will be commercialized.

6. Magma. Pools of molten rock or magma at temperatures of 650°C and higher are known to exist in or beneath volcanoes. Numerous chambers of magma formed at the corners of subduction zones also are believed to have gradually ascended to various depths beneath the surface. The number of such pools is speculative, and few are actually known except in Hawaii and Alaska. Indirect evidence suggests the existence of a large silicic magma chamber (45,000 km^3) beneath Yellowstone Park, which, after cooling a million years, still retains 67,000 quads of thermal energy. A magma body 5 km thick, with slab-like geometry, would require 2 million years to cool by conductive heat loss to ambient temperature.

The CONAES report, after excluding magma bodies in national parks or below 6 km depth, and further assuming that only 1 percent of the accessible heat content will be recovered as useful heat above 80°C, estimates that only 35 quads of such energy can be produced.

Methods by which accessible magma pools may be tapped for useful energy are being investigated, but no drill hole has yet penetrated a deep magma chamber. Successful penetration requires good control of the system at the high temperatures and pressures likely to be encountered--a situation akin to controlling the energy of a minivolcano. Yet the development of such a system offers the prospect of large quantities of high-temperature energy potentially useful as process heat or process steam now provided by use of fossil fuels, as well as electricity generated with higher thermodynamic efficiency than is attainable from heat sources at lower temperature. The potential benefits warrant intensive research and development directed toward the penetration of deep-lying magma and the utilization of magma thus entered.

D. Problems Retarding Fuller Utilization of Geothermal Energy

Regions of crustal instability or deformation run in several belts around the Earth: one (known as "the ring of fire") extends around the continental margins of the Pacific, including Alaska and the western United States, Mexico and Central America, Japan, the Philippines, and New Zealand, and another from the Indonesian islands across the middle of Asia and through southern Europe. It is in these belts, which are characterized by recent or current volcanism or other tectonic activity, that most of the major hot hydrothermal areas are found.

The hot springs, geysers, and fumaroles that are the surface evidence of underground hydrothermal systems have been documented for 2100 years, but aside from their use for bathing, which attracted outsiders to spas, they were exploited as a source of heat only where the need occurred close to the hydrothermal area. Thus, during the 19th century, geothermal steam was used in Italy for heating and to run stationary steam engines, and, early in this century, to drive a turbine providing electricity for local use. A well-insulated pipe in Italy has transported hot water 100 km for over 10 years with 98.5 percent thermal efficiency; in Iceland, geothermal hot water is piped efficiently for over 40 miles. But for the most part, geothermal energy in the form of steam or hot water has been used only when three conditions were met: outward manifestations of the presence of geothermal energy, a near-by need, and no cheaper available source of the needed energy. When these conditions have been met, the uses of geothermal steam and hot water have been varied: city space-heating, greenhouse heating, air-conditioning, Frasch-process sulfur mining, process steam for paper mills, drying of timber and agricultural crops, drying of minerals, and many similar operations utilizing low-grade heat. The generation of electricity by geothermal steam has been practiced in many countries for three quarters of a century but is still but a tiny fraction of the world's total electrical output. In some countries, geothermal energy development was interrupted when natural gas or other fossil fuels were discovered.

Only when geothermal energy is freed from the three conditions of use just mentioned can it become a major factor in supplying the world's energy needs--when geothermal sources can be tapped for use wherever they are needed, at costs competitive with those of other energy forms. To attain this objective, emphasis must be placed on developing means for recovering geothermal energy from resources more broadly abundant and offering the prospect of recovering heat at higher temperatures than are normally possible from hot water and steam reservoirs. Geothermal heat could then be used directly for industrial purposes and for efficient generation of electricity, thus permitting expansion of the use of electricity for such large-scale purposes as space heating and the powering of electric automobiles, at competitive power costs.

The widespread use of abundant geothermal energy resources hinges, then, on the development of feasible methods of energy recovery from hot dry rock, from magma, from geopressurized brine, and, ultimately, from normal-gradient sources. Many problems must be solved to implement such a program, as well as to utilize geothermal steam and hot-water resources more fully. While solutions to most of these problems involve engineering, applied physics, and applied chemistry, basic chemical research in many cases can provide an underpinning of data and theoretical understanding that might expedite the developmental programs undertaken.

This report will not attempt to define the myriad of specific problems calling for basic chemical research. Instead, several broad problem areas are listed below and discussed briefly, with the recommendation that basic research proposals bearing on progress in any of these areas should be seriously considered for support by DCS.

1. A number of legal, political, and social handicaps to the further development of geothermal energy affect both its economy and its social acceptability. The environmental impact of the installations is a major consideration: geothermal installations may intrude on the aesthetic character of an area, may affect wildlife, in some cases (when large volumes of underground water are withdrawn without replacement) may cause sinking at ground level, may induce earthquakes by underground changes of pressure at critical balance-points of faults, may release radioactive isotopes such as radon, which have accumulated underground, or build up radioactive daughters of radon decay on the exposed surfaces of plant equipment, and may cause emission of gaseous pollutants (CO_2, H_2S, NH_3) as well as waterborne pollutants undesirable in downstream drainage (alkali chlorides, sulfates, silicates, ammonium salts, borates, fluorides, and occasionally arsenic, antimony, mercury, thallium, and even gold and silver). Tests of water from steam at The Geysers, however, have shown that the amount of alpha radiation (1.5×10^{-9} mCi/ml) is well below U.S. Public Health Service permissible levels. Processes for removal of gaseous contaminants are known, and additional DOE-funded research directed toward improved processes is in progress. Similarly, techniques for the removal of waterborne impurities are known and are likely to be further improved by continuing research.

2. Geothermal energy plants are capital-intensive, and costs related to well-drilling (particularly if the wells are deep) may constitute 60 percent or more of the total investment. Wells for geothermal installations are generally drilled with techniques used in the oil and gas industry. The deepest drill-hole yet has been about 9 km and its cost (1974) was $667,000 per kilometer. More recent costs are approximately $1.5 million per kilometer. In many studies of geothermal potential (e.g., the CONAES report), 6 km is considered a practical limit. Greater use of geothermal energy would be favored by the development of new drilling techniques that would be cheaper and/or would permit drilling to greater depths, to 10 km and perhaps even 15-20 km, with sufficient control to permit bottom-hole fracturing if desired. New, more controllable fracturing methods, either chemical or physical, are also needed. Such capabilities would permit tapping of hotter geo-

thermal layers, and even in normal-gradient areas would permit recovery of thermal energy at above 300°C and perhaps as high as 600°C.

A host of related research and development projects is embodied in such a program. New drilling materials are needed that would withstand the higher temperatures and pressures, and possibly more corrosive environments: drillbits, drilling fluids, muds, high-temperature logging devices and means for transmitting the logged information (including high-temperature elastomeric insulating materials for logging cables), seals, valves, cements, heat shields, and means for transmitting and isolating cuttings and core samples from such depths. In particular, exploration should be encouraged of radically new well-forming techniques that are not merely adaptations of present oil- and gas-drilling methods (see Chapter 10, Polymer Chemistry, Section IIID). Research on new drilling technology has been carried out at the Sandia and Los Alamos National Laboratories, and in Japan, but more is needed.

3. Corrosion and scaling continue to present problems, particularly with brines of high concentration and waters containing hydrogen sulfide. Although progress has been made toward their solution, more research is needed on methods for removing the offensive agents, on additives to prevent scale deposition and corrosion, and on alloys that resist corrosion and erosion without sacrifice of other desirable properties. Information is needed on the high-temperature diffusion of hydrogen sulfide though elastomeric cable coatings. It would be helpful to understand more fully the mechanism and kinetics of silica, limestone, and metal-sulfide deposition from supersaturated, hot geothermal waters undergoing cooling and/or concentration.

4. New concepts should be explored for converting subsurface heat to on-surface energy in usable form. Methods now used--direct use of water as a carrier or a double fluid system with heat exchange--are adaptations of conventional chemical engineering practice. Are there other methods more efficiently adaptable to dry rock beds under the temperature, pressure drop, and distance constraints of geothermal systems? Can the "total flow" concept of Lawrence Livermore National Laboratory, which operates turbines on the kinetic energy of a mixture of water, steam, and solids arising from the depressuring of geothermal brines, be further improved as a practical means of using such resources?

5. Although considerable information has already been amassed, much remains to be discovered about the properties and behavior of rocks in strata at geothermal depths, particularly during the operations of site preparation and removal of heat. Areas for investigation include the mineral composition of virgin geothermal deposits, the high-temperature solubility of such minerals and the hydrothermal changes taking place during circulation of hot water, the composition and properties of secondary minerals formed by hydrothermal recrystallization, and the dynamics of hydraulic fracturing and thermal stress-cracking of rock formations of various types. Some laboratory simulations and theoretical studies of such systems have been carried out; more should be encouraged.

TABLE 2. Distribution of DOE Geothermal R&D Funds

	1980	1979
	(Dollars in Millions)	
Hydrothermal resources programs*	59.0	70.9
Resource definition	9.0	25.5
Facilities	32.9	28.6
Engineering applications	9.8	10.5
Regional planning	6.1	5.8
Environmental control	1.3	0.5
Geothermal technology development	43.9	57.6
Component development	24.9	36.8
HDR activities	14.0	15.0
Interagency coordination	2.9	4.3
Capital equipment (instrumentation)	2.1	1.5
Resources development	6.3	0.3
Personnel resources	1.9	1.7
Geopressurized resources**	36.0	27.7

* Classifications overlap.
** Budgeted under Energy Technology/Fossil/Gas.

E. DOE Support of Geothermal Research

Of its total budget of $3,583 million for Energy Technology in FY 1980, DOE allotted $111 million (3 percent) to geothermal technology, down $19 million or 15 percent from 1979. Allotments to specific programs for the two years are described in Table 2.

In the Basic Research area, $1.5 million was requested in 1980 for Geochemical Engineering in the geothermal area (60 percent less than in 1979), $69.4 million for all of Basic Research in Chemical Sciences (26.6 percent more than in 1979), and $10.8 million in Geosciences, including Geochemistry (up 77 percent from 1979). Few projects related to geothermal energy are funded by DCS.

In view of the potential of geothermal energy as an indigenous, abundant source of energy, its development merits acceleration by an infusion of considerably more funds by DCS, as well as by other divisions of DOE.

9. ELECTROCHEMICAL ENERGY

I. INTRODUCTION

Modern electrochemical research is mainly concerned with charge transfer across interfaces and the accompanying chemical and physical processes. The interface is frequently that between a metal electrode and a liquid or solid electrolyte where electron transfers occur. However, electrodes of carbon, semiconductors, and other conductive materials are also important, as are studies of ionic transport at interfaces (e.g., at membranes) or in bulk phases. Electrochemistry is clearly concerned with the interconversion of electrical and chemical energy and hence with electrical power generation by fuel cells and primary batteries and energy storage in secondary batteries. An important advantage of electrochemical systems for generation of electricity is the potentially high efficiencies obtainable for the conversion of stored chemical energy to electricity, because these devices, unlike heat engines, are not Carnot cycle-limited. These systems will be directly involved in electrical energy storage, electric power load-leveling, solar-energy electricity, electric vehicle propulsion, and some systems for converting heat to electricity (thermally regenerative emf cells or electrochemical engines). However, electrochemistry is also involved in electrosynthesis (e.g., the industrial electrolytic production of chlorine and aluminum), electroplating and electrorefining, control of corrosion and pollution, and electroanalysis. While these applications are involved less directly with energy conversion, they may be of great importance in attempts to improve overall utilization and conservation of energy. For example, the total electrical energy in the United States consumed in industrial electrolytic processes (such as production of Al, Cl_2, Cu, Mg, Na, chlorates) is in excess of 2×10^{11} kWh/year, or about 10 percent of the total electric energy generated. Improvements in process efficiencies could result in major savings of electric power. Electrolyzers may play an important role in the production of fuels (e.g., H_2 from water electrolysis or methanol from CO_2 reduction) and in processing of materials.

The development and improvement of electrochemical systems and devices applicable in energy-related areas will best be served by a program of basic research in electrochemistry along with more applied studies. Basic studies could lead to needed breakthroughs, for example in the development of an efficient, inexpensive metal catalyst for oxygen reduction, or an alkali metal-electrolyte system capable of undergoing multiple electrodeposition-stripping cycles, which could have major impact on the manufacture of practical fuel cells or high energy-density storage batteries. New concepts are emerging in the design of electrochemical cells, such as redox flow storage batteries utilizing soluble reactants (where external storage and extended cycle lives are possible) and new electrode materials (intercalation compounds, organic metals, polymer electrodes). Such developments can emerge only from continued investigation of the nature and behavior of the electrode-electrolyte interface and the processes occurring there.

The important general areas of basic research in electrochemistry are discussed below in the following categories: electrode kinetics and electrocatalysis, surface structure of electrodes, descriptive electrochemistry, electroanalytical chemistry, thermodynamic properties and mass transport, and photoelectrochemistry. Specific recommendations on research are summarized in Section II immediately following, and the areas are discussed in depth in Section III under Discussion.

II. RECOMMENDATIONS

Research in the electrochemical field is recommended as follows:

- o Studies of the fundamental factors controlling charge transfer reactions at interfaces and the development of new electrocatalysis (e.g., for O_2 reduction and for H_2 and fuel oxidation).
- o Studies of the detailed structure of the electrode surface and of adsorbed reactants and intermediates, including the development of *in situ* methods of investigating the interface.
- o Development of new electrode materials (e.g., of conductive polymers, organic metallic conductors, semiconductors) and methods for the purposeful modification of electrode surfaces (e.g., through polymer layers, adsorption, covalent attachment).
- o Development of electroanalytical methods and electrochemical sensors.
- o Studies of electrocrystallization phenomena and factors affecting electrode surface morphology during deposition and stripping.
- o Investigations of the energetics, kinetics, and mechanisms of potentially useful electrode reactions (e.g., CO and CO_2 reduction, O_2 reduction, H_2 and hydrocarbon oxidation, alkali metal deposition, solution redox reactions).

III. DISCUSSION

A. Electrode Kinetics and Electrocatalysis

Research in electrode kinetics is aimed at obtaining a detailed understanding of the rates and mechanisms of charge transfer reactions at interfaces and the effect of the chemical and physical nature of the interface on these. Electrochemical catalysis is part of the broader field of heterogeneous catalysis and involves the use of electrode surfaces that promote specific electrochemical reactions by providing sites favorable for the adsorption of reactants, products, and/or intermediates, besides serving as a source or sink for electrons in the charge transfer steps. Examples of electrode processes involving electrocatalysis are the oxidation of hydrogen and the reduction of oxygen in fuel cells where high-area electrocatalysts such as platinum on carbon are used to accelerate the reactions. The catalysis of the hydrogen oxidation reaction is quite satisfactory, but no comparably effective electrocatalyst for the oxygen reduction has yet been found, so that present fuel cells and air-consuming batteries operate at voltages well below the theoretically attainable.

Many other electrochemical reactions appear attractive for batteries or fuel cells with higher energy density if catalysts can be found to enhance their rates. Among the possibilities are the direct electrochemical oxidation of methanol, ethanol, and synthetic hydrocarbons. In a similar vein, better electrocatalysts are needed to facilitate solar-energy harvesting by electrochemical devices such as liquid-junction solar cells based on semiconductor electrodes.

Further research in the following areas would help to promote the discovery and exploitation of new electrocatalysts and extend knowledge about the rates and mechanisms of electrode reactions:

1. Charge Transfer at Interfaces: Theory, Kinetics, and Mechanisms. Theory, experimental criteria, and chemical documentation for electron transfers at interfaces via inner-sphere mechanisms are primitive in comparison with outer-sphere cases and to solution chemistry. The relative importance of tunneling, entropic factors, and enthalpic energy barriers to electron transfer at interfaces is unsettled, both theoretically and experimentally, and the temperature dependence of most electrode reaction rates is unknown. Since many useful electrocatalytic reactions may be inner-sphere, these topics need increased attention. Also, modern spectroscopic methods may be exploited to detect fast and poorly understood electron transfer steps in multielectron reactions.

The application of modern theoretical methods to interfaces, and particularly to the electrode/solution interface, is a virtually untouched area. Although this area is clearly very difficult, increasing power of computational methods and hardware may allow it to be studied. If theoretical treatments with predictive power can be coupled interactively with experimental studies, so that they provide more than a simple justification or formalization of known results, important advances are possible in understanding the interface at a molecular level.

2. Electrode Material, Surface Structure, Morphology: Effects on Kinetics. The adsorption of species at the electrode-solution interface may affect the rate and pathway of an electrode reaction (e.g., tetraalkyl ammonium ions on many organic reactions, halide ions

on corrosion of iron). This is in part an inner-sphere phenomenon (i.e., involves a specific interaction with the electrode surface). To correlate such effects with inner-sphere theory, it will be necessary to couple modern electrode-surface characterization experiments with kinetic studies. Efforts are needed to relate the electrocatalytic studies carried out under ideal laboratory conditions (with ultra-pure and well-controlled systems) to the real world of electrocatalysis where long-term operation in impure systems is required. Particular areas of study should include the effects of adsorbed impurities, of the size and morphology of catalyst particles, of the nature of the catalyst supports, and of the wettability of the surfaces.

The coupling of electrode kinetics to mass transfer and potential gradients in microporous electrodes is important in electrocatalysis and in corrosion phenomena, and not only improved theory but better microporous model surfaces are needed.

3. Adsorption on Electrocatalysts. Adsorption isotherms and adsorption-desorption kinetics should be established for a wide range of adsorbed reactants and intermediates. Information is needed as to how the adsorption is related to the electronic and morphological properties of the surface as well as to properties of the electrolyte. Comparative studies of adsorption on the same type of surfaces in vacuum and in electrochemical environments should also prove useful in understanding electrocatalysis, particularly on metal surfaces such as platinum and gold where the interaction of the surface with water is weak.

4. New Electrocatalyst Systems. Promising approaches include electrode surfaces modified to accept and hold catalytically active species, metals deposited as monolayers or less on inactive supports, metal atoms implanted in matrices, and addition of catalysts to gaseous reactants fed to electrode surfaces. An expanding variety of redox sites can be affixed to the surfaces of conducting and semiconducting electrodes in monomolecular and polymeric multilayer forms. The kinetics and mechanisms of electron transfer and transport at these interfaces need better understanding, both fundamental and as applied to the design of optical state situations as in electrochromics. A great potential exists for novel catalytic modified surfaces, but adequate criteria for selection of redox states and theoretical catalytic models are needed.

5. Heterogeneous and Homogeneous Electrocatalysis. Evaluation of the merits of electrocatalytic schemes based on charge transfer mediation by heterogeneous versus homogeneous chemical states will require study of relative kinetics, stability, and specificity of mediator reagents over a broad front. Additionally, the maturing field of homogeneous transition-metal catalysts is largely untapped for electrocatalytic purposes because involvement of specific electron transfer events in the operation of such catalysts is not well understood. Moreover, kinetic studies of homogeneous electron-transfer reactions and the complex-ion dissociation and association reactions that often

accompany them are needed, as part of the orderly evolution of the background chemistry essential to understanding the corresponding heterogeneous electrochemical reactions. Complex-ion dissociation kinetics plays an important role in electroplating and in certain fuel cell and battery systems. Detailed kinetic data on such processes is essential.

B. Surface Structure of Electrodes

Direct investigation of electrode surface structure is essential to development of electrodes and elucidation of reaction sequences for energy efficient electrochemical devices. Critical areas for future study are:

1. Electrode Surface-Structure Determination. Data regarding the atomic and molecular structure of electrodes and on the change of the nature of the surface with time are virtually nonexistent, and reliable information as to the composition, identity, quantity, orientation, chemical properties, and influence of molecules present at electrode surfaces is in short supply. Such data can be obtained for single-crystal electrodes by low-energy electron diffraction during exposure to electrolyte vapor and following electrolytic processes, and then can be correlated with cell performance. External methods such as Auger, photoelectron, and mass spectroscopy should be utilized, as well as *in situ* techniques based on thin-layer electrochemistry, optical spectroscopy, radiochemistry, and microanalysis. Lack of knowledge of surface and overlayer structure at present thwarts understanding and optimization of electrode performance in fuel cells, batteries, electrocatalysts, photoelectrochemical cells, and related devices. Electrode-surface molecular chemistry is central to developing the technology for future energy systems of an electrochemical nature.

2. Electrocrystallization and Electrode Morphology. New techniques for determining the structure and composition of electrode surfaces can lead to an increased rate of progress on the important problem of electrocrystallization. Early studies were hampered by a lack of methods for surface characterization of the substrates and deposits. Progress in this area is now possible and can lead to immediate improvement in the quality and production efficiency of numerous substances and materials now produced or refined electrolytically.

3. Passivation. The chemical changes in structure, morphology, electronic state, and composition, accompanying electrochemical stabilization of practical surfaces need characterization. Data for well-defined but realistic materials and conditions are in short supply. Progress in this area can prevent or counteract vastly expensive destruction of metallic objects by corrosion, cracking, and related processes.

C. Descriptive Electrochemistry

To achieve adequate technological performance in devices for the production and storage of energy, one must generally have rather complete knowledge of chemical details. Lack of knowledge implies a lack of control. Failure mechanisms and low efficiencies attributable to poor kinetics usually stem from poor understanding of mechanistic features and side reactions. Research in descriptive electrochemistry, with an emphasis on mechanistic understanding, is essential to further progress in the development of practical systems.

Part of the effort should go to careful work with processes important to immediately recognizable technology, such as the reduction and evolution of molecular oxygen, the oxidation and evolution of hydrogen, electrode reactions of hydrocarbons and alcohols that could be useful in fuel cells, electrode reactions producing feedstocks from CO or CO_2, and processes important in a variety of batteries for energy storage. Of particular importance is the oxygen reduction reaction. If good kinetic behavior for this process could be achieved at an economic electrode, energy-efficient fuel cells would be practical in short order.

Continued research with reactions at "classical" electrodes, such as Pt, Au, and other metals, should be supported, if they promise to elucidate the general features of reactions. On the other hand, practical systems will have to be based on other types of electrodes, such as carbon, oxide films, base metals, or semiconductors, any of which may be modified by catalytic agents. Real advances in applications of electrochemical processes to energy technology require imagination, which means that the conventional reactions must be examined in new situations, involving new surfaces and catalysts. It also means that wholly novel electrochemistry ought to be studied for possible use in new technology. Synthetic organic and inorganic chemistry are now in a productive period and offer new materials of clear interest, especially as catalysts. Electrochemical explorations of their behavior should be encouraged.

Some important specific areas deserving attention are as follows:

1. Basic Electrochemistry of Energy Conversion. Research is needed on simple electrode reactions of high-energy reagents such as alkali metals, halogens, and fuels; electrochemistry of small, potentially plentiful species such as oxygen, hydrogen, CO, CO_2, water, and H_2O_2; electrochemistry in molten salts and nonaqueous media. Some specific electrode reactions deserving detailed study include:

a. O_2 reduction: The reduction of O_2 to water and hydroxide ions is the cathodic electrode reaction in fuel cells and metal-air batteries. The O_2 is usually derived from air. O_2-consuming electrodes also offer promise for substantial electric energy savings in industrial electrolytic processes such as the generation of chlorine and caustic through brine electrolysis. The reduction of O_2 in aqueous electrolytes, however, is a quite irreversible process even with the best catalysts available, despite extensive investigation over the past 35 years. Until recently the search for improved catalysts has been mostly empirical and not effective. Mechanistic details of the O_2 reduction need to be pinned down and a predictive base established for the identification and optimization of catalysts. New approaches to the problem should be encouraged (e.g., the use of bimetallic transition-metal complexes, chemically modified electrode surfaces, underpotential-deposited layers of foreign metal).

b. H_2 oxidation: The only successful fuel cells are those operating on H_2 as the fuel. The oxidation of pure H_2 proceeds with relatively little voltage loss on platinum and platinum-family catalysts. Since most H_2 originates from hydrocarbon sources, however, carbon monoxide is usually present as a substantial impurity, which has forced the use of temperatures above 150°C and restricted the choice of electrolytes. High-performance, lower-cost alternatives to platinum-family catalysts are needed for the oxidation of H_2 in the presence of CO in acid electrolytes. To this end, basic research should be directed to understanding the mechanism and kinetics of the H_2 electrode reactions, and the adsorption of reaction intermediates as well as the adsorption of CO and its oxidation on various electrode surfaces. Supporting theoretical studies of these adsorbed species and proton transfer reactions at electrochemical interfaces should also be encouraged.

c. Oxidation of hydrocarbons and alcohols: The oxidation of a hydrocarbon or alcohol in fuel cells offers promise of much higher energy-conversion efficiency than is obtained with heat engines. However, catalysts of sufficient activity have not been identified for these oxidation reactions with aqueous electrolytes. On such a catalyst as platinum, the reaction is highly irreversible and oxidation does not go quantitatively to completion, with the result that partially oxidized species accumulate in the cells. The oxidation does proceed reasonably well at high temperatures in molten salt and solid electrolyte cells, but there are severe problems of materials stability. Little progress has been made in the oxidation of methanol and hydrocarbons in fuel cells since the 1960's, and new ideas are needed.

d. Electrosynthetic reactions: As natural gas and liquid hydrocarbon reserves become depleted, electrochemistry offers the possibility of synthesizing hydrocarbons and other organic feedstocks (e.g., methanol, formaldehyde, glycols) from CO_2, CO, and even coal; for example, the synthesis of CH_3OH from CO_2 could proceed at a cathode:

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$

in the overall cell reaction

$$CO_2 + 2H_2O \rightarrow CH_3OH + \frac{3}{2}O_2.$$

If the proper catalyst can be found, such electrosynthetic methods could be particularly attractive, utilizing electrical energy derived from solar or nuclear sources. The critical element is the electrocatalyst.

e. Key electrode processes in battery systems: While a number of the battery systems now under development for vehicle and load-leveling applications have been known for many decades, much uncertainty persists concerning the mechanisms of the electrode reactions and in some instances even the overall cell reactions. Oxide electrodes are used in many cells, but the role of solid-state transport processes versus solution-phase processes is not well understood. Morphological changes and dendrite formation are often problems, particularly with zinc and lithium electrodes. The factors controlling O_2 and H_2 generation as competing electrode processes on various battery electrodes also need to be established.

Many electrode reactions for battery application appear attractive on paper, but practical considerations interfere with their use (for example, slow kinetics, physical problems associated with incorporating the reactants in battery electrodes, competing reactions). With the introduction of new solvent-electrolyte combinations, electrode structures, and membranes, some of these reactions may prove practical.

2. Descriptive Electrochemistry of Electrocatalytic Systems. To support the basic studies of the nature of electrocatalysis discussed in Section IIIA, new chemistry applied to possible catalytic systems should be investigated. This includes electrochemistry of homogeneous catalysts that can be attached to electrodes by surface modification, studies of suspended particulate redox catalysts, electrochemical studies with catalytic micellar and other organized chemical systems, and descriptive electrochemistry of metal complexes, organometallics, and aromatics.

3. Solid-State Chemistry and New Electrode Materials. Studies should be addressed to solid-state ionic conductors, electrointercalation chemistry, electronically conducting polymers and molecular solids as electrodes, thin-film electrodes of oxides and alloys, carbon as an electrode material, and descriptive electrochemistry of semiconductors, including single crystals, polycrystalline samples, and suspended particles. The studies should include polymers as modification agents for electrodes, redox properties of polymers, and polyelectrolytes.

D. Electroanalytical Chemistry

Electroanalytical chemistry is concerned with the measurement, analysis, and control or monitoring of chemical systems. Chemical systems cover a wide range from simple aqueous systems to such hostile environments as oceans, molten salts, chemical processing streams, and fluids surrounding nuclear cores. Goals are the identification and characterization of major and trace-level components. The chemical systems studied by electroanalytical chemistry are generally in the liquid state, but application to solids has been made, use in gas analysis is growing. The importance of analytical chemistry in energy-related research was discussed in Part 1 (see Appendix B). Areas of electrochemistry important as applied to chemical analysis are discussed here.

1. Electrochemical Sensors. Research is needed on electrochemical sensors, such as species-selective electrodes and systems employing electrochemically sensitive methods for determining environmentally noxious gases. Such sensors, which must be capable of sustained operation in the surroundings, particularly at high temperatures, have widespread application in monitoring both processes and environmental contamination. Combination of electroanalytical and nonelectrochemical techniques (see below) has resulted in the development and understanding of new sensors.

2. The Development of New Instrumentation and Techniques. This requires detailed understanding of the fundamental processes involved in a technique, developing instrumentation to carry it out, and establishing how it works, its limitations, and advantages. Past efforts have resulted in methods that have been applied to studies important not just to electroanalysis but to catalysis (rotating disk studies applied to underpotential deposition), and studies of surface phenomena at photoelectrochemical and modified electrode surfaces (pulse and cyclic voltammetry, chronocoulometry). Future developments in electroanalytical techniques will likewise find application not only in electroanalysis but in areas important to a variety of energy-related areas, including battery systems. Development of electroanalytical techniques today goes hand in hand with development of new methods for studying the details of electrochemical mechanisms, instrumentation involving use of microcomputers and minicomputers, new methods for signal processing (various new transform methods), and the like.

3. New Electroanalytical Methods. Method development is a requirement for the application of any analytical technique but is particularly important in electroanalysis where complex and interfering reactions must be studied and understood to permit utilization. Electroanalytical methods tend to be highly dependent on the sample environment, and elucidation of the fundamental, often complicated underlying chemistry of the sought-for constituent and interferences is most important. Method development often tends to be overlooked, because it is time consuming and not overly glamorous, but it is absolutely vital to the solution of a particular, defined problem where an electroanalytical method may well be more sensitive, suffer fewer interferences, and be less costly than other competing methods. Besides, electroanalytical methods of certain kinds are well suited to automation, remote operation in isolated areas, and flowing systems where multiple sensors can monitor constituents changing in concentration with time.

4. Coupling of Electroanalytical Techniques with Nonelectrochemical Methods. This is a rapidly developing area that will con-

tinue to grow and become even more important. An example is the coupling of spectrophotometry and various electroanalytical methods (cyclic voltammetry, pulse voltammetry, thin-layer electrochemistry) into spectroelectrochemistry, useful for the study of fast reactions in homogeneous solution, absorbed and entrapped surface entities, modified electrodes, and photoelectrochemical systems. Other examples are combinations of electroanalytical methods with a host of surface spectroscopic techniques (LEED, Auger, ESCA, etc.). Most recently, the discovery of the enhanced Raman effect at certain electrode surfaces has resulted in a large amount of research to understand this effect and has cut across both chemistry and physics. Also of great current interest are efforts to develop electrochemical detectors for liquid chromatography.

Thus, electroanalytical chemistry is widely useful, not only in and of itself, but across the entire spectrum of electrochemical research and indeed in many areas outside of electrochemistry. Perhaps the most striking example is cyclic voltammetry, which, developed to full potential less than twenty years ago, now is employed in a fairly routine manner by inorganic, organic, and physical chemists, as well as many others in nonchemical areas.

E. Thermodynamic Properties and Mass Transport

Basic research in energy must be strengthened by broadening the scientific understanding of electrolytic systems. Research on thermodynamic and transport processes is critically important for this purpose.

Nearly every DOE program is impacted by electrochemical phenomena in one form or another. Most of these phenomena are sufficiently complex that existing knowledge is insufficient to guide technological improvement. A purely empirical approach would hold scant promise for cost-effectiveness. Improved understanding of electrochemical fundamentals and development of a reliable data base are vitally important. Basic research areas in need of attention are:

1. Aqueous and Nonaqueous Solvent Systems. Fundamental knowledge of thermodynamic and transport properties of solutions is essential for developing more effective energy conversion and storage systems. Improved predictive capability based on such knowledge will be particularly useful in identifying and exploiting electrolytic solutions showing high conductivity, rapid mass transport, and other desired properties. Current theories are virtually incapable of predicting properties of most industrially important electrolytic solutions.

2. Molten Salt and Solid Electrolyte Systems. These systems offer the highest energy density for battery applications but present severe stability problems (e.g., cracking of ceramic separators in sodium-sulfur cells). Improved basic understanding is essential for achieving high conductivity at lower temperatures where corrosion is less severe. Research on the development and behavior of low-temperature molten salts, for example, offers promise. The potential impact of improved understanding of these systems is truly enormous.

3. Properties and Transport in Membranes. Much effort is needed to understand charge transport across ionic membranes. The potential for new breakthroughs is enormous. Membranes are important components in many electrolytic processes and often represent a major factor both in investment cost and operating (power) cost. Fundamental research should be encouraged on low-resistance membranes exhibiting stability, selective transport properties, and low cost.

4. Modeling Electrochemical Systems. Mathematical models based on first principles are important because they promote orderly arrangement of knowledge in complex systems, they define scale-up criteria, and they assist in establishing mechanisms. Central to all electrochemical energy systems is the need to articulate design criteria for achieving large reaction rates in small volumes. Optimization of porous electrode structures is critically important in battery systems and in emerging electro-organic synthesis options. Re-optimization of aluminum and chloralkali systems is urgently needed to accommodate rapid emergence of new technological developments. Development of new formulations for electroplating baths offers promise of conserving critical resources by imparting desired surface properties to inexpensive substrate materials.

5. Data Base. A common need pervading all energy technologies is access to a reliable data base. Thermodynamic, kinetic, and transport properties must be known if rational scientific methods are to be used to develop improved systems. Collection, collation, and critical evaluation of existing data should be a part of research and development efforts. Discrepancies and knowledge gaps should be identified, and critically sparse regions must be strengthened. Development of cost-effective predictive methods based on reliable data would exert tremendous leverage on future research effectiveness.

F. Photoelectrochemistry

Research on the interaction of light with electrochemical systems has been especially active in recent years. Developments in this field could lead to systems for the utilization of solar energy for the production of electricity, fuels, or useful chemicals. This topic is discussed in Chapter 7.

SECTION IV: Research Needs in Selected Fields

10. POLYMER CHEMISTRY

I. INTRODUCTION

The purpose of this chapter is to consider the contributions that polymers can make to various energy options and the basic chemical research needed to support the contemplated developments. An important and distinguishing feature of polymer research is that, in its very essence, it is interdisciplinary. The chemical, physical, engineering, and material science aspects of polymer research cannot be disentangled, as witnessed by the fact that polymer research is largely done in interdisciplinary polymer research institutes at a number of universities and in interdisciplinary industrial or government laboratories.

One outstanding feature that makes polymers attractive for many applications is their potentially favorable strength-to-weight ratio. This is illustrated by the new high-strength aromatic polyamides (e.g., Du Pont "Kevlar" aramid fiber) and composites embodying them. For instance, the specific tensile strength (the tensile strength divided by the density) of "Kevlar" is about five times that of steel and more than ten times that of aluminum.

On an equal-volume basis, manufacture of many polymers consumes less energy than metal manufacture, even when the energy equivalent of the chemical feedstock is taken into account. Thus, production of a given volume of polyethylene requires only a fifth of the energy expended for the same volume of aluminum, or a third of that for steel.

Besides the applications specific to certain technologies, two needs recur again and again in the discussion to follow. These are for polymeric construction materials of outstanding strength, on the one hand, and of greater resistance to environmental stresses, such as high temperature and pressure, aggressive chemical conditions, and radiation of all kinds, on the other. Research should be aimed at the acquisition of fundamental knowledge to support the development of polymeric materials of ever higher strength and stability, as discussed in this chapter. In the quest for polymers of long-term stability, a further basic need is the development of accelerated aging test methods validated by comparison with unaccelerated test results.

Feedstocks derived from coal will contribute an increasing share of the available hydrocarbon raw materials. To the extent that their chemical compositions may differ from those of petroleum feedstocks, there is need to adapt present processes and to develop new methods for the synthesis of monomers from the coal-derived feedstocks. Indeed, new monomers--and consequently new polymers--may well become technically and economically feasible.

In assembling this chapter, the authors have made use of the DOE publication, Polymer Materials--Basic Research Needs for Energy Application, Proceedings of a Workshop Recommending Future Directions in Energy-Related Polymer Research, June 27-29, 1978, at Case Western Reserve University, Cleveland, Ohio, edited by W.J. MacKnight, E. Baer, and R.D. Nelson (CONF-780643 UC-25). This publication covers a number of the topics in much greater detail than is possible here and is a valuable resource for matters that touch on energy-related uses of polymers. Further relevant information can be found in a special issue of Science (No. 4446, Vol. 208, May 23, 1980), which is completely devoted to advanced-technology materials.

Before proceeding with discussion of basic research needs, it is appropriate to mention that the polymer field has developed in a manner quite different from the typical scientific discipline in that much of the pioneering basic research in the United States was done in industrial laboratories (e.g., in the 1930's by Carothers at Du Pont and in the 1940's by Flory at Du Pont, Goodyear, and Esso). This tradition continued for many years, with a large portion of the fundamental work done in industry while polymer science blossomed and polymer manufacture grew into the enormous industry of the present.

During the past quarter century, polymer science found a precarious foothold in the universities, with the research done largely by individual professors or small groups in chemistry and related departments and by a few interdisciplinary institutes. This situation is reflected in the small number of institutions granting degrees in polymer science (38 grant Ph.D. degrees, including 18 granting degrees in traditional disciplines with specialization in polymers) and the almost complete absence of polymer-related courses in most chemistry departments.

Even at the present time relatively little polymer research is done in chemistry departments (a 1978 survey found that fewer than 2 percent of the faculty members in the 20 leading graduate chemistry departments had research interests primarily in polymer science). A somewhat greater and growing effort is taking place in chemical engineering and material science departments (the same survey found that in the 10 leading chemical engineering departments 16 percent of the faculty had polymer research interests). It is significant that many of the faculty active in polymer science spent an appreciable part of their early careers in industry.

There are a number of indications that the basic polymer science research effort in U.S. industry has been decreasing during the last decade as companies turned to more applied research and development. There are few signs that academic institutions are taking up the slack. Moreover, judging by the number of publications and patents issued, the United States is slipping in relation to other countries, especially Japan and those of Western Europe.

A joint *ad hoc* Panel of the Committee on Chemical Sciences and the

Solid State Sciences Committee of the National Research Council is currently examining the state of basic research in polymer science and engineering in the United States. We expect its conclusions to have relevance to the present report, and we urge the Division of Chemical Sciences to consider those conclusions carefully.

II. CONCLUSIONS AND RECOMMENDATIONS

The discussion to follow makes it abundantly clear that polymers can make ever-growing contributions to many facets of the energy field. Many opportunities exist for basic research that can pay dividends in terms of progress in all phases of the energy industry. Such progress is going to be optimized only if the underlying theories and facts are being developed at an increasing rate. The Department of Energy has a considerable stake in technological developments in polymers, and, consequently, OBES should support basic research in polymer science.

Following are several specific conclusions:

- There are important needs for polymeric materials of outstanding strength and greater resistance to environmental stresses, such as high temperatures and pressures, aggressive chemical conditions, and radiation. Meeting such needs will require the discovery and development of new polymers, polymeric composites, and various types of protective systems.
- There is a need for better basic understanding in most aspects of polymer science. Specific areas include morphology, adhesion, stability, and structure/strength relationships.
- In the use of polymers for many energy-related applications, there is a particular need for the understanding of aging phenomena and the development of accelerated test methods that simulate real aging conditions.

III. DISCUSSION

A. Energy Conservation

Polymers have the potential of making important contributions to energy conservation. For instance, the weight reductions needed in automobiles and other vehicles will be achieved only by substitution of high-strength, lightweight materials for metals. The most promising of these materials are based on plastics. The use of polymeric materials in automobiles has already increased greatly, doubling between 1972 and 1980 to roughly 100 kg per vehicle (exclusive of tires), and this trend is expected to continue. Development of improved polymer-based structural materials will be aided greatly by elucidation of the relations between the intramolecular and intermolecular polymer structure, on the one hand, and mechanical and failure properties, on the other. A number of new tools for polymer structural studies have become available recently, as for instance high-intensity x-rays, solid-state NMR, and the various laser-based optical methods, and their full potential remains to be exploited.

Another potentially fruitful field is the systematic investigation of polymer-based composite materials, which comprise not only structures made up of plastics and elastomers containing reinforcing elements such as wire, fibers, and fine-particle mineral fillers but also blends of polymers and indeed materials made up of segmented molecules that segregate into separate phases on cooling from the melt. The theory of composite structures is largely undeveloped, and much basic research needs to be done. One promising area is study of the interfaces between the phases that make up the composites. Improvement in the understanding of the interfacial forces and their effects on the mechanical properties of the composites should lead to stronger and more versatile materials. Similarly, much more needs to be known about the dependence of the composite properties on the morphology, i.e., the supramolecular structure of the constituent polymers. Compatibilizers, materials such as graft copolymers, that act between polymer phases like surfactants between liquids of low molecular weight, can change morphology and interfacial forces greatly, and only a small beginning has been made in the quantification of their effects.

Better fundamental understanding of polymerization kinetics and diffusion in viscous systems can lead to improved process control in polymer synthesis, enhanced product quality, and hence less waste. Such savings are also the aim of the search for new analytical methods and new polymerization catalysts, as well as energy-efficient polymer isolation methods, e.g., the potential use of membranes to isolate the polymer from its polymerization medium.

Better insulation of domestic and commercial structures is an essential objective for energy conservation, and polymeric foams will play an increasingly important role in this field. The kinetics of foam formation and the choice of reagents employed in foaming will be reflected in the foam structure (size and size distribution of cells, cell wall thickness, gas contents of cells, continuity or discontinuity of cells), which in turn will influence the heat-transfer properties. Thus, studies of the basic chemistry and kinetics of foam formation are needed to optimize insulation properties and to solve a number of outstanding problems of certain organic polymer foams: the tendency of foams to shrink away from the surrounding structure, the possibility of toxic vapors emanating (as, for instance, free isocyanates from polyurethane foams), the flammability of the foams, and the possible liberation of toxic gases on combustion.

Reduction of losses in the transmission of electrical power is another requirement for which polymers will be increasingly useful especially as covers for electrical cables. For instance, research is already under way to replace the conventional high-loss kraft paper insulation on high-voltage underground power cables with low-loss polymers such as polyethylene. Treeing phenomena in plastic insulating materials are not well understood, and explanations of the chemical processes occurring during such electrical breakdown would be of great help in the search for additives and/or purification procedures that improve the electrical properties of high-voltage insulating materials.

Many opportunities for energy savings exist in the fabrication and processing of polymers. A longer useful life for plastic and rubber articles requires greater resistance to degradation by heat, atmospheric components, and radiation. Such less easily degraded polymers will also permit material economics by recycling processing wastes and discarded articles. The search for more resistant polymeric materials or additives that confer such resistance would be aided greatly by improved insight into the chemical processes that occur when polymers, especially state-of-the-art highly resistant ones such as perfluorinated, aromatic, and inorganic polymers, are exposed to strenuous environments. Model compound studies could be helpful in such programs.

Energy-efficient polymer fabrication methods include reaction injection molding (RIM), in which low-viscosity components are reacted during the molding process to give finished polymeric parts, thus obviating the need for the energy-intensive processing of high-viscosity polymers. Development of the full potential of RIM requires fundamental chemical studies of the reaction systems currently employed and those of potential applicability. For conventional polymers, investigations of the effect of molecular weight distribution and backbone structure on the rheological properties could point the way toward reduction of the energy required for processing.

Conservation of hydrocarbon feedstocks is also the aim of increased usage of natural and of inorganic polymers, which may provide a better combination of properties and cost, as well as use of abundant by-products, such as CO and SO_2, as components of new copolymers. Organic polymers still contain a large part of the caloric content of the feedstocks from which they are made. Much of this can be recovered by using fabrication wastes and worn-out polymeric articles as fuels for generating steam. Studies of polymer combustion chemistry should aid in the development of furnaces capable of burning such fuel without undesirable environmental impact.

B. Enhanced Oil Recovery

Only 20-30 percent of the total crude oil present in the typical oil field is accessible by the conventional production methods. The remainder resides in the pores of the oil-bearing formations. Enhanced oil recovery (EOR), discussed in detail in Chapter 5, deals with the liberation of as much as possible of the remaining 70-80 percent. Under favorable economic conditions, perhaps a quarter to a third of this is amenable to currently envisaged methods of EOR, which involve "flooding" of the oil fields: injections into special wells of suitable pressurized fluids that carry the oil toward the producing wells. Such methods are already in wide use in U.S. oil production, but much potential for improvement remains.

The fluids used for EOR are generally aqueous solutions. To achieve maximum effectiveness, the displacing solution must have a viscosity greater than the petroleum to be displaced. To this end, suitable polymers are added to the injected water in order to raise its viscosity. Thus water-soluble polymers are needed that effect large viscosity increases at low concentrations. So far, a few commercially available polymers (polysaccharides and acrylamides) are under consideration for this application and are being field tested, but much basic research remains to be done, as exemplified below.

Studies are needed of the behavior of polymers in dilute aqueous solution under the stressful conditions to be encountered: high temperatures and pressures, dissolved salts, acidity or alkalinity. New polymers will have to be sought that are especially well adapted for EOR, i.e., that can survive these stringent conditions as well as confer high viscosities at low concentrations.

Fundamental reseach, both experimental and theoretical, is needed on the rheological behavior of polymer-thickened aqueous solutions, especially with respect to their flow through porous media. Since surfactant solutions are often used to precede the polymer solutions, more detailed knowledge will have to be accumulated on polymer-surfactant interaction in aqueous media as well as on adsorption of polymers from aqueous solution.

It is also essential to develop laboratory tests capable of predicting polymer performance under field conditions in order to make screening of candidate polymers practical.

C. Solar Energy

The use of solar energy encompasses a great variety of approaches (described in Chapter 7). The techniques considered here are solar thermal energy conversion, direct photovoltaic energy conversion, and wind energy conversion. In all of these techniques, polymers, because of their unique properties, play a variety of roles. They will be needed as structural materials, adhesives, coatings, and encapsulants in solar components, wind energy converters, and energy storage devices. In addition, there will be a need for polymeric heat-transfer fluids.

Much knowledge remains to be collected for the optimum utilization of the polymers in these applications. Basic research should be carried out on photodegradation of polymers and model compounds, and detailed understanding of these processes could well lead to more effective photostabilizers. The permeability of relevant polymers to gases, especially potential degradants like H_2O, O_2, SO_x, NO_x, O_3, needs to be studied from theoretical and practical points of view, as does the interaction between polymers and metals such as occurs in coatings.

Since all solar applications envisage extended use, information is needed on the long-term thermomechanical and viscoelastic behavior of structural components and heat-transfer fluids and on how these properties are affected by the chemical changes that occur as polymers age. Little is know about the molecular changes occurring when polymers are exposed to repeated deformation and long-term stresses. Progress in this area is needed. Applications of polymeric adhesives and sealants will be furthered by basic studies of the chemistry of adhesion, surfaces, and the effects of additives.

The chemistry of polymer surfaces needs to be studied from the point of view of deterioration by radiation and environment, soiling, and dust accumulation, knowledge of which will have impact on use of polymers as collector covers, refractive and reflective concentrators, light receivers, and encapsulants.

D. Geothermal Energy

While the drilling of geothermal wells appears similar to the drilling of oil and gas wells, the conditions encountered are apt to be much more strenuous (see Chapter 8). Materials are required that can survive the high temperatures and pressures likely to prevail, and they must be resistant to water containing saline and gaseous solutes (methane, CO_2, H_2S). Material costs are not very significant in any deep drilling activity since failure of a small part deep down a hole can often only be remedied by many hours of expensive maintenance operation. In this area, therefore, one can contemplate the use of high-cost esoteric polymers of outstanding performance characteristics.

Polymers will be needed for seals, gaskets, packings (especially elastomeric packer seals installed between well wall and drill pipe), electrical insulator coatings, corrosion- and erosion-resistant coatings, and scale-release surfaces. Elastomers have been developed over the years that are capable of withstanding more and more demanding conditions, culminating in the currently available perfluoroelastomers, fluorosilicones, and polyphosphazenes. However, ever more stringent conditions are likely to be encountered in drilling, logging, and maintaining geothermal wells, and development of even more resistant polymers will have to rely on fundamental studies in a number of different fields. For this purpose, greater basic understanding of structure-property relations of polymers, especially elastomers, under conditions of high temperature and pressure needs to be acquired (see also Section I of this chapter).

Research is also required on the effects of high temperature and water pressure on those polymer properties that govern the electrical behavior of insulating polymers (e.g., those used to cover the instrument wires in well logging). Efforts to develop polymeric coatings that provide abrasion resistance and inhibit scale formation are needed and will require studies of the fundamental properties of polymer surfaces.

Research is also needed on concrete-polymer and fiber-reinforced polymer composites in order to exploit their impermeability, toughness, favorable strength/weight ratio, and corrosion resistance.

E. Energy Storage and Conversion

Effective energy storage systems would have the potential of making more efficient use of available energy sources. A great variety of devices can be envisaged, ranging from pumped storage hydroelectric systems to small batteries.

Flywheels are under consideration for energy storage in vehicles and solar/wind machinery. In automobiles, they would make possible the recovery, storage, and reuse of braking energy; such an application would be particularly attractive in electric cars. To be practical, the flywheel must be made of a material with the capacity of storing a large quantity of kinetic energy per unit mass. Fiber-reinforced plastic materials can be several times more efficient in this respect than steel. Much progress remains to be made and calls for greatly increased knowledge of the behavior of high-strength polymeric composite structures, specifically of their morphology, failure phenomena, stress fields, and toughening mechanisms.

Electrical batteries are the most common storage devices at present, but much more efficient batteries are needed for practical vehicular and other uses. Many different chemical principles are under consideration for battery use; a number of them envisage anode and cathode compartments separated by membranes. Another form of energy storage is in electrolytic hydrogen, which might be produced from hydroelectric sources not suitable for high-voltage power generation. Membranes made of perfluoropolymer and containing carboxyl and/or sulfonic acid groups can be used in "solid polymer electrolyzers" and thus introduce a new and potentially much more efficient technology. Basic research into the functioning of these materials will be needed to attain their maximum potential in batteries and electrolytic cells. Membrane research might also benefit reverse osmosis processes for desalination of seawater and recovery of gases besides hydrogen, e.g., CO, SO_2, H_2S.

A number of applications are envisaged for thermal energy storage. For instance, it has the capability of greatly extending the usefulness of solar energy. Phase transitions provide one way of thermal energy storage, and crystalline polymers are among suitable materials. Thus, studies of phase transitions in existing or especially tailored polymers should be undertaken. Furthermore, polymers should be considered for encapsulation of nonpolymeric materials with thermal storage capacity, such as salt hydrates.

Superconductive magnets are under consideration for high-efficiency rapid-access energy storage at power plants. High-strength polymer composites might find application in structural members of these large storage plants. A speculative goal of immense potential benefit is the discovery of polymeric superconductors, the ultimate aim being to find materials that are superconductive at temperatures above the extremely low ones needed for present superconductors. Further research on the energy levels and conduction mechanism in polymers known to be highly conductive will be essential to progress in this field.

F. Nuclear Reactors--Operation, Reprocessing of Fuel, Waste Disposal

There are many conventional and unconventional applications for polymers in the nuclear industry. Two special material requirements stand out: extraordinary reliability and resistance to high-energy radiation.

Polymers are used in all the conventional chemical process applications in nuclear generating and fuel reprocessing plants, e.g., pump packings, valve seals, hoses. Much more knowledge needs to be acquired on the degradation of polymers by radiation, especially in the simultaeous presence of thermal, pressure, and chemical stresses. The effects of such degradation on mechanical properties, failure mechanisms, permeability to gases and liquids, etc., need to be studied and related to polymer structure. The resulting findings should be helpful in the development of new, more radiation-resistant polymers and of additives that enhance stability in the presence of radiation. Polymeric coatings and films capable of containing low-level solutions for extremely long periods are needed in facilities for reprocessing and waste storage.

Reprocessing of nuclear fuels involves ion separation, and polymeric ion exchangers are prime candidates for such applications. While polymeric ion exchangers have been used for a long time, new materials are now becoming available that can be fabricated into membranes, tubes, and other shapes that lend themselves to more efficient continuous operation than the conventional beads. To take full advantage of these possibilities, more fundamental information is needed on the permeation of ions through such materials as a function of polymer structure, pore size distribution, nature of the ion-exchange sites, etc.

Immobilization of radioactive wastes is involved in a number of long-term disposal schemes. While most of these currently envisage inorganic immobilization matrices, polymeric materials may have a useful role to play. Synthesis of polymers with strong ion-binding sites is needed for evaluation in this application.

G. Fusion

Use of polymeric materials is contemplated in structural and insulating components of fusion and fusion/fission hybrid reactors as well as in fuel pellets for inertial confinement fusion.

Such applications require the same kinds of knowledge as a number of the uses discussed earlier: e.g., effects of radiation (especially that from tritium) and high-temperature exposure, and development of high-strength, low-weight structural materials. However, the extraordinary conditions prevailing in fusion devices give rise to special requirements. One area of concern for polymers at low temperatures is the "Wigner catastrophe," i.e., the avalanche-type release of stored energy triggered by radiation.

Insulating materials for use in superconductive magnets must be able to survive extremely low temperatures and extremely high magnetic, electrical, and radiation fields. Moreover, they must remain functional after repeated temperature cycling between ultralow temperatures and ambient conditions. The effects of such cyclic exposure must be investigated, especially with regard to retention of insulating properties in the presence of liquid helium. Under such conditions, crazing and crack formation could lead to electrical breakdown.

Fabrication of inertial confinement fusion targets will employ polymers as coatings and foams. Coating methods need to be developed that are suitable for this use. Target fabrication employing polymeric foams will be aided by studies of the rheological behavior of foams of very low density.

11. CATALYSIS

I. INTRODUCTION

Since most reactions that occur in high yield upon merely mixing reactants at some reasonable temperature and pressure have probably already been discovered, future improvements in chemical transformations will be largely catalytic. Indeed, catalytic processes already dominate the petroleum and petrochemical industries and are of major importance in the chemical industry. Catalytic processes involve a cycle in which the catalyst enters into reaction with the reactants and is regenerated at the end of the cycle. The overall rate of product formation is larger in the presence of the catalyst than in its absence and, in most useful cases, very much larger: one unit of catalyst can lead to the formation of many units of product.

Catalysts offer the potential of carrying out chemical reactions more efficiently or, in most cases of industrial interest, of carrying out chemical reactions that will not occur at practicable rates in the absence of a catalyst. Thus, catalysis is intimately involved in most aspects of increasing the effectiveness of the production and utilization of energy from chemical sources, including fossil fuels. The escalating costs of such sources and of capital during the past decade have put a greater premium than ever on efficiency. Since catalysts enable chemical transformations to be carried out not only more rapidly, in higher yields (i.e., in higher selectivities), and at lower temperatures, but also often in a single step instead of several, the potential savings in energy and capital costs in an industrial process can be enormous.

Fossil sources, i.e., coal, oil, and natural gas, will continue to provide the major portion of energy for transportation until the end of the century. And as coal liquids, shale oil, tar sands, and heavy oil become more prevalent as refinery feedstocks, catalysis will be even more challenged to resolve problems of selectivity, operating and capital costs, and operating flexibility to meet market demands.

In searching for catalysts, the paramount concerns are catalytic activity (promoting faster reaction), selectivity (increasing the yields of desired products and reducing the costs of separation), and stability (leading to long life, resistance to poisons, and easy regeneration of the catalytic system, with attendant reduced operational costs). A further concern is characterization, to define so far as possible the precise characteristics of the catalyst and of the complexes it forms with the reactants.

The following aspects of catalysis are particularly important to DOE:

1. The interconversion of chemical energy forms. Catalysis, particularly heterogeneous catalysis, is involved in nearly all aspects, beyond preliminary distillation, in converting conventional and nonconventional fossil feedstocks into various fuels and chemicals, and in removing undesirable constituents like sulfur, nitrogen, and oxygen.
2. Energy conservation, particularly in the chemical process industry. Better catalysts and better catalytic processes can provide important savings in the industrial consumption of fuel.
3. Conservation of materials. Catalytic processes improve efficiency of the use of feedstocks for fuels and chemicals. Their selectivity enables, for example, the conversion of methanol to gasoline or other desired hydrocarbon products in high yield, and also increases the efficiency of coal hydrogenation.
4. Reduction of pollution. Catalysis will permit combustion of lean mixtures of fuel with air at lowered temperatures, thus reducing the formation of NO_x.
5. Catalyzed photochemical and electrochemical conversion and storage of energy. These topics are discussed elsewhere in this report, but we note here that photochemical conversion includes utilization of solar energy and that electrochemical conversion and storage include fuel cells.

Catalysis is customarily classified in the three categories: homogeneous, heterogeneous, and enzymatic. It is a fair assessment to state that homogeneous catalysis is relatively well understood in terms of substituent chemical processes constituting a reaction mechanism, even though the details may not have been established in individual cases. Until recently, heterogeneous catalysis was far less well understood in that characterization of the interfaces at which reaction presumably occurs was extremely difficult; new experimental methods of surface analysis offer promise of resolving this difficulty and thereby of opening the way to systematic design of superior heterogeneous catalysts. Enzymes play an important role in a variety of industrial processes, alcoholic fermentation being among the most prominent. Considerable progress has been made by biochemists and molecular biologists in determining the structures of selected enzymes and correlating their precise architecture with their remarkably efficient and selective catalytic activity. Enzymes present a challenge in what can be accomplished in the design of a catalytic system, and recent research has focused on various metal complexes that come close to mimicking enzymatic activity. Genetic engineering utilizing techniques of recombinant DNA offers promise of producing specific enzymes on a commercially viable scale.

The practical importance of new concepts in catalyst development, aside from the intrinsic scientific interest, cannot be overstressed. The development of molecular-sieve-based catalysts, for example, in place of traditional silica-alumina catalysts has had a profound impact on the industrial processing of hydrocarbons, including the production of gasoline and benzene from methanol.

II. SUMMARY

- Future energy supplies, utilization, and conservation are inextricably tied to the greater and more effective utilization of catalytic processes.
- Although oil, coal, and natural gas are expected to remain the principal sources of energy for many years, alternate sources for the production of liquid fuels will be even more demanding with respect to use of catalytic processes.
- Homogeneous catalysis will probably not be involved in large-scale upgrading of oils but should find extensive utilization in the production of chemicals and petrochemicals from synthesis gas. It is likely to contribute also to conservation of energy in the chemical process industry.
- Whereas homogeneous catalysis is largely the domain of inorganic and physical organic chemists, heterogeneous catalysis involves input from nearly all facets of chemistry and chemical engineering, from material science, and from surface chemical physics. Thus, in many cases, research on energy conversion processes will be utilizing a highly interdisciplinary approach. Indeed, certain projects are not likely to be successfully attacked except by collaborative efforts.

III. SPECIFIC DISCUSSION

Both heterogeneous catalysis and homogeneous catalysis are and will be important in energy-related matters. Other things being equal, the simplicity and economy of the heterogeneous catalytic reactor (in particular, the absence of a catalyst recovery step) makes a heterogeneous catalytic process inherently more economical than a homogeneous one. However, other things are not always equal. A homogeneous catalyst may provide greater selectivity than any known heterogeneous catalyst. Probably more important is the fact that the heterogeneous catalytic process appears in its most attractive form only for processes using adiabatic reactors, that is, reactors in which heat neither enters nor leaves the reactor. Consequently, an exothermic reaction that needs to be run at lower temperatures for reasons of selectivity or catalyst stability may be less well suited for a heterogeneous than for a homogeneous catalytic process. Thus, there are active and selective heterogeneous catalysts for the hydroformylation of olefins,

$$RCH{=}CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO$$

but, as far as we know, only homogeneous catalysts are used industrially.

If a homogeneous catalytic process, for example,

$$CH_3OH + CO \rightarrow CH_3COOH$$

on a rhodium catalyst, is adequately understood, one simply has a sequence of well-characterized reactions of organometallic complexes in which the catalytic species is reformed after a cycle of reactions. Thus, since homogeneous catalysis is apt to remain a subspecialty of coordination and organometallic chemistry, support for the basic science of homogeneous catalysis must, in part, be support for much of those chemical subdisciplines.

In the same sense, the "catalysis" in heterogeneous catalysis could become an aspect of surface chemistry. However, adequate understanding of the surface processes constituting the catalytic cycle is more remote than comparable understanding in homogeneous catalysis. The problems are complicated and difficult and, as a consequence, research in heterogeneous catalysis remains more interdisciplinary than does homogeneous catalysis. At present, surface chemistry has fewer practitioners than either organometallic or coordination chemistry.

With a few exceptions, academic research in the area of homogeneous catalysis is carried on in departments of chemistry. On the other hand, academic research in heterogeneous catalysis in the United States is carried on primarily in departments of chemical engineering. Only a few members of chemistry departments work in heterogeneous catalysis. This absence of interest on the part of most chemistry departments impedes U.S. academic accomplishment in heterogeneous catalysis. Although some problems could be equally well studied in either a chemistry or a chemical engineering department, and some would be more appropriate in a chemical engineering department, other important areas are more likely to be studied in a chemistry department. The detailed surface mechanisms of heterogeneous catalytic processes is one such area. In general, research involving substantial background in organic and coordination chemistry is less likely to be undertaken in chemical engineering departments; graduate students in chemical engineering are usually not inclined toward problems dealing with chemical synthesis or complicated molecules.

Heterogeneous catalysis is treated quite differently in academic institutions of several other countries with significant effort in the area. It is studied in departments of chemistry in France, the Netherlands, and Japan. The major Japanese universities have two or more research groups in heterogeneous catalysis in their chemistry departments besides groups in their engineering faculties.

In addition to much of conventional chemistry, heterogeneous catalysis involves solid-state chemistry and physics, physical chemistry, surface chemistry and surface chemical physics (surface science), and mass and heat transport problems. Collaboration should be fostered between members of chemistry and chemical engineering departments working in various areas of heterogeneous catalysis and workers in such other areas as surface chemical physics, inorganic chemistry, and materials science. Such collaborative efforts will normally entail research budgets larger than are usual for projects administered by a single principal investigator.

Although few areas of heterogeneous catalysis are without interest to DOE, several warrant particular attention. A key need is additional knowledge about the detailed mechanisms of heterogeneous catalytic reactions: identification of the surface intermediates and elementary surface processes composing the overall catalytic cycle. Without such information one cannot optimize catalytic processes by means of modeling nor can one properly interpret correlations of catalytic activities and selectivities with characteristic properties of the catalysts. In some reactions of hydrocarbons, considerable information exists about the identity of the hydrocarbon portion of the absorbed intermediates of the catalytic cycle. However, little is known about how the hydrocarbon intermediates are bound to the surface of the catalyst and about the energy changes involved in the absorption. Thus, for example, little is known about why platinum and palladium give different rates and selectivities as catalysts in a number of these reactions.

Little is known about the details of elementary surface reactions in general. Progress in ameliorating this situation is likely to be slow, but support for research here is a key need, and, as the section immediately following explains, surface chemical physics and organometallic chemistry are apt to contribute importantly.

In the United States, research on heterogeneous catalysis is heavily concentrated in Group VIII metals. These metals constitute important catalysts, but a larger fraction of effort should probably be directed toward other kinds of catalysts. And many studies in heterogeneous catalysis could be improved by more careful comparison of results with those of previous work, improved control of experimental variables, and additional attention to the influence of heat and mass transport on catalytic rates and selectivities.

IV. SURFACE CHEMICAL PHYSICS

Surface chemical physics (SCP) is an independent field of science with important bearing on heterogeneous catalysis. SCP may be of interest to the Office of Basic Energy Sciences for its potential contribution to fields other than heterogeneous catalysis, for example, to the understanding of corrosion. However, only its possible contributions to heterogeneous catalysis are described here. SCP deals mostly with the surface of single crystals of pure chemical substances fabricated to expose a particular crystallographic face as ideal as possible. The aspects of SCP of potential application to heterogeneous catalysis are studies of chemisorption and of reactions of chemisorbed species with other chemisorbed species and with molecules from the gas phase.

Practical catalysts are complicated materials. Rarely is anything known about which crystallographic faces are exposed and their relative proportions. Often, the faces exposed are not those of pure chemical substances, and often two or more phases are present. From the standpoint of heterogeneous catalysis, 99.99 percent platinum (Pt) with an average particle diameter of 2 nm supported on pure silica gel would be one of the simplest catalysts. From the standpoint of SCP, it would be a very complicated material.

For heterogeneous catalysis, interest in SCP arises from the hope that the study of simple systems can provide information unobtainable in studies on practical catalysts but leading to a theoretical framework applicable to useful systems. It should be possible, for example, to determine separately the exact structures of CO on several nearly ideal crystal faces of Pt far more readily than to determine the structures of the variety of adsorbed species of CO on the Pt particles of the Pt/SiO_2 catalyst mentioned above.

Historically, SCP arose from work in ultrahigh vacua (UHV), and the techniques developed in SCP usually necessitate the use of UHV. Often, SCP employs a beam of electrons as a probe, or electrons leaving the sample as a signal--sometimes both. In low-energy electron diffraction (LEED), a beam of electrons is diffracted from the surface of a crystal. The wave properties of the moving electrons result in a diffraction pattern analogous to that in X-ray diffraction, although extraction of complete structural information is more difficult in LEED. LEED analysis reveals the surface structure of the original, clean crystal face and, with much more difficulty, the structure of chemisorbed layers (provided that they are ordered, which they often are). With time, we can look forward to an inventory of detailed structures of chemisorbed layers on various crystal faces of various solids important in catalysis. Two entries would be CO and C_2H_4 on Pt (100) in which the exact structure would be described, just where each atom of the absorbate was located, and the distances from surface atoms. For any but the simplest system, the problem is not easy, but substantial progress is being made.

In another technique, high-resolution electron energy loss spectroscopy (EELS), a beam of low-energy electrons is reflected from a surface containing a chemisorbed layer, and the energy distribution of the reflected electrons is measured. Electrons can excite vibrational modes of the adsorbate and lose energy in the process. The information obtained resembles that from infrared spectroscopy. The combination of LEED and EELS can provide important information about the structure and chemical nature of chemisorbed layers.

LEED and EELS have been chosen arbitrarily as examples of the techniques employed in SCP. However, they do exemplify the intrinsic power and limitations of SCP as applied to the problems of heterogeneous catalysis. The power has been described above. Limitations include the necessity of working at UHV; bombardment by electron beams may alter the nature of a chemisorbed layer, particularly when the layer is organic; the adsorbed layer studied is necessarily one that does not desorb in UHV, whereas in heterogeneous catalysis the pressure is one or more atmospheres and catalysis is ineffective unless desorption--at least that of the product--is fast. However, techniques have been developed that serve, at least in part, to bridge what has been called the pressure gap. The exact correlation to be expected between the (100) face of a bulk single crystal of Pt and a (100) face of a 2-nm particle of Pt is unclear at present. Some organometallic chemists are working at explaining the chemistry of such tiny particles by extrapolating up from the chemistry of cluster compounds containing from 6 to 20 atoms of metal. It is not yet clear whether the closest approach to the truth will come through extrapolation from bulk crystals down to 2-nm particles or from cluster compounds up. However, one may suspect that both approaches will contribute to the picture eventually emerging.

SCP will certainly not solve all the problems of heterogeneous catalysis, and some areas will not soon profit from knowledge gained through SCP (for example, the chromia-on-silica catalyst used in the polymerization of ethylene). However, SCP has already contributed to advancing our understanding of catalysts involving metals of Group VIII and appears particularly promising as a route to understanding other important catalysts. Basic research along the following lines would be particularly useful to progress in heterogeneous catalysis:

1. Determination of established surface structures of chemisorbed layers on substances of catalytic interest, i.e., on Pt, Pd, or Rh, for example, rather than on W. Improved procedures are needed for avoiding damage to chemisorbed layers during measurement.
2. Studies of interactions among adsorbed species, or between molecules in the gas phase and adsorbate molecules, that is, contributions toward identifying, classifying, and understanding the adsorbed intermediates of heterogeneous catalysis and of the elementary processes they undergo.
3. Thermodynamic studies of the structures and processes described in 1 and 2.
4. Studies of nonmetals, oxides, for example. Such insulators have been little studied because the electron probes or signals cause charging. The electric field distorts the signal. Progress in this area could be rewarding.
5. The nature of poisoning, deactivation, and promotion at the molecular level.

12. MISCELLANEOUS SELECTED TOPICS AND DISCIPLINES

A. Organic Chemistry

Although this report is not structured according to the classical divisions of chemistry, it may be useful to make one exception and single out organic chemistry. For historical reasons, DOE has not given this discipline the support needed for an efficient basic research effort in energy science. The precursor agency, AEC, had a mission that required relatively few organic chemists and consequently not much support went into organic chemical research. However, a broadly based energy program cannot avoid making heavy use of organic chemists. Clearly, coal research, synthetic fuels, solar-energy conversion and storage, and photosynthesis research all depend heavily on input by synthetic and physical organic chemists.

Among the many areas of organic chemistry, one that should receive attention is physical organic chemistry, a discipline most likely to have an impact on energy research. The chemistry of free-radical, excited-state, and ionic reactions in the gas phase is directly related to combustion and solar-energy conversion. The field of catalysis, homogeneous and heterogeneous, is the basis for synthetic fuels and coal liquefaction. Energy storage via reversible organic reaction should not be ruled out as a possible practical solution to the problem. Determination of the structures of coals is a problem in organic chemistry calling on all the traditional tools of organic structure determination, including modern spectroscopic techniques such as pulsed NMR in the solid state. The chemistry of heterocycles is also directly related to the coal problem. Organic electrochemistry is connected with fuel cells, and research in this area is bound to have an impact on solar-energy conversion as well. These are just a few examples to point out that a large fraction of modern energy research is based on organic chemistry and that support of basic research in organic chemistry is entirely appropriate for DOE.

B. Separation Processes

Separation processes have assumed steadily increasing importance in many technological areas, such as petroleum refining, petrochemicals, nuclear fuel preparation and recycling, water purification, air pollution control, coal preparation, and minerals upgrading and processing. Several factors have contributed to this importance:

1. The sharply higher recent values of all petroleum-derived materials have made it economically attractive to develop separation processes providing higher yields of purer products;
2. The growing scarcity of many raw materials, ranging from minerals and biological products to potable water, has spurred the development of more efficient separation processes;
3. Increased fuel costs are stimulating improvements in the energy efficiency of separation processes;
4. Pollution control regulations have led to the invention of separation systems and devices for both fixed sources and vehicles, as well as to improvements in existing processes: scrubbing, catalytic, and mechanical and electrical removal in gas streams.

Advances to date do not begin to satisfy needs. For example, no economically attractive desulfurizing system for flue gas has yet reached the development stage. No chemical system has been devised that can produce valuable products, such as concentrated sulfuric acid or SO_3, in a reliable, economical way.

Separation processes were studied in a fundamental way by creative chemical engineers during the early years of the nuclear power industry. There is a need and a potential for innovation, both in improvement of processes now in use and in development of new processes, in the light of the basic principles of separation. Even a process as thoroughly studied as distillation, subjected as it has been to computerized optimization with respect to economic performance, capital costs, and energy consumption, can be improved by new designs coming from re-examination of its thermodynamic underpinnings. In the direction of less understood processes, there are methods and applications that call on the special skills of the chemical community. The use of supercritical conditions to effect separations by small changes in the system exemplifies a method with broad potential application. Separation of liquids from capillary channels in solids by use of selective surfactants, a process touching on many areas of chemistry, is an approach both interesting as a general method and vitally important for two immediate needs, the separation of hydrocarbons from rock in tar sands and EOR (see Chapter 4 and 5). An area where the problems rather than methods of separation dominate the issues is the separation of nuclear waste products for recovery and disposal.

Other new or improved separation techniques include diffusion, centrifugation, laser activation, use of selectively permeable supported membranes or hollow fibers, reverse osmosis, large-scale chromatography, sorption on size-selective or shape-selective zeolitic or other solids, nonconventional liquid-liquid and liquid-foam extraction systems, ultrafiltration, electrostatic and electrophoretic systems, and chelation.

For many of these, the theory and basic information underlying their operation are incomplete and imperfectly understood. Fundamental research on the kinetics, thermodynamics, equilibria, and structural factors operative in such systems is needed and could well provide the understanding that would lead to greatly superior separation processes. OBES should continue to be alert to research proposals likely to provide such understanding.

C. Nuclear Waste Disposal and Decontamination of Nuclear Facilities

The problem of proper disposal of radioactive wastes from nuclear power production is one of the important obstacles to the continued or expanded utilization of nuclear energy. Although solutions that are considered acceptable in several countries have been found, their adequacy has been questioned. This is an area where an intensive research effort is warranted.

At least four stages of containment can be utilized to assure that the radioactive wastes do not present a health hazard to current or future generations. The first stage depends on the stability and inertness of the host material (glass or crystalline material) for the radioactive species. Much work suggests that various glasses have sufficient stability. But further studies to optimize the composition of the glasses from the standpoint of, e.g., containment of leachable radioactive species, are certainly in order.

The investigation of crystalline host minerals is a particularly promising area of research. The possibilities here range from a universal host (such as UO_2) that has demonstrated radiation stability and inertness in a nonoxidizing environment to specially synthesized minerals that will specifically incorporate the most important radioactive elements.

A second stage of confinement is represented by the containers for the radioactive wastes. Materials used must be inert in conditions expected and conceivable in a geological setting, and over geological times; they must also be economically practical.

In the third stage, the migration of the important radioactive elements in a natural environment (assuming that the first two barriers fail) should be evaluated. This involves understanding the solubilities and adsorption of the important radioactive elements by natural minerals. The retentive characteristics of the natural surrounding medium can be enhanced by backfill with material chosen to hold up the migration of the most dangerous radioactive species, as well as to provide more choice of mechanical characteristics in the local environment.

Finally, the behavior of the dangerous elements in the natural food chain of animals and plants must be understood.

Such studies, covering as they do a significant fraction of the periodic table, are bound to provide not only a basis for evaluating the risks involved in a particular solution to the problem of disposal of radioactive wastes but important understanding of natural processes in nature on the surface of the earth. Research here will involve material science, geochemistry, and engineering but will have a large component of chemistry. Strength in the closely related subdisciplines, nuclear chemistry and radiochemistry, must be maintained to provide needed basic knowledge of the properties of the many elements present, in varying amounts, in spent nuclear fuels. This information base supports changing technological approaches to fuel reprocessing and waste disposal.

The potential contributions of advances in separation processes to the solution of nuclear waste disposal problems should be kept in mind. These include methods for extraction of actinides from spent fuel. These elements have been found to be the principal cause of long-term deterioration of mineral or glass host media and represent the major cause of health hazard at intermediate times following waste disposal. New separation methods have the potential for improving the economics of reprocessing by making possible the extraction of valuable, scarce, essential metals, some of which must now be imported.

A related problem of increasing importance is the decontamination of materials following nuclear operations or accidents. This has recently been highlighted in extreme form by the Three Mile Island incident but will have to be faced even in routine operations of nuclear facilities as well as in the normal course of decommissioning of nuclear facilities (reactors or even accelerators). The technical problems here center on the development of effective and practical complexing agents for the most dangerous radioactive species. This will make possible their removal from important equipment or from the environment, and their concentration for appropriate disposal. Similarly, the establishment of chemical conditions to retard the plating out of trace radioactive species in pipes, pumps, etc., during routine operation can significantly extend the useful life of existing nuclear facilities.

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Section I: Research Needs in Selected Fields

Section II: Research Policy Issues . . . .

APPENDIXES

APPENDIX C. CONTRIBUTORS

The ad hoc Panel on DOE Chemistry Research of the Committee on Chemical Sciences is responsible for this report and any inadequacies in its recommendations. But the Panel is pleased to acknowledge its indebtness to the thoughtful and, in some instances, extensive contributions from colleagues listed below.

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