Molecular Energy and Environmental Science

A Workshop Sponsored by

The National Science Foundation
and
The Department of Energy

May 26-27, 1999
Rosemont, Illinois

Organizer: Peter C. Stair, Northwestern University

Co-Chairs: Joseph M. DeSimone, University of North Carolina, Chapel Hill
John W. Frost, Michigan State University

Participants:

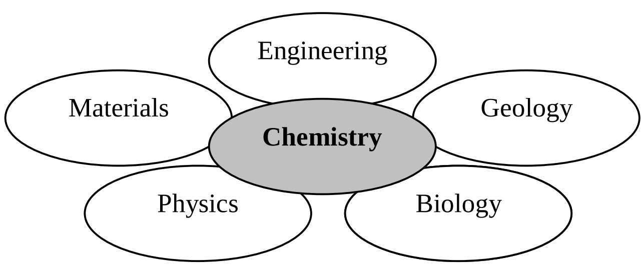
Gordon E. Brown, Jr., Stanford University
Carol J. Burns, Los Alamos National Laboratory
Margaret Cavanaugh, National Science Foundation
Steven D. Colson, Environmental Molecular Science Laboratory
Galen E. Fischer, Delphi Automotive Systems
George W. Flynn, Columbia University
Joseph S. Francisco, Purdue University
Jeffrey S. Gaffney, Argonne National Laboratory
Robert J. Hamers, University of Wisconsin, Madison
Tomas Hudlicky, University of Florida
Dan Meisel, University of Notre Dame
William S. Millman, Department of Energy
François M. Morel, Princeton University
Janet R. Morrow, State University of New York at Buffalo
David L. Nelson, National Science Foundation
Paul H. Smith, Department of Energy
Eugene S. Smotkin, Illinois Institute of Technology
Francis A. Via, General Electric Company
John H. Weare, University of California, San Diego

Executive Summary

Energy and the environment pose major scientific and technological challenges for the 21st century. New technologies for increasing the efficiency of harvesting and utilizing energy resources are essential to the nation's economic competitiveness. At the same time, the quality of life in the United States depends inherently on the environmental impact of energy production and utilization. This interdependence makes it imperative to develop a better understanding of the environment and new strategies for minimizing the impact of energy-related activities. Recent advances in techniques for the synthesis and characterization of chemicals and materials and for the molecular control of biological organisms make it possible, for the first time, to address this imperative.

Chemistry, with its focus on the molecular level, plays a central role in addressing the needs for fundamental understanding and technology development in both the energy and environmental fields. Understanding environmental processes and consequences requires studying natural systems, rather than focussing exclusively on laboratory models. Natural systems and their complexity pose an enormous, perhaps the ultimate, challenge to chemists, and will provide them with varied and exciting new problems for years to come. In addition, the complexity of the underlying systems and processes often requires multi-disciplinary programs that bridge the interfaces between chemistry and other disciplines. (See Figure 1) This has ramifications in the approach to funding research and suggests needs for broadening the educational training of future scientists and engineers in these programs.

Figure 1.



NSF and DOE should consider sponsoring research centers and focused research groups organized to optimize their impact on **Technological Challenges** of national interest. The research will have significant impact if it addresses issues of fundamental molecular science in one or more **Enabling Research Areas**. Approximately 7 research centers and 40 collaborative research groups are needed at a total annual funding level of $30 Million.

Technological Challenges

1. Energy
2. Chemical Synthesis & Processing
3. Clean Air
4. Clean Water
5. Clean Earth

Enabling Research Areas

A. Materials Synthesis & Nanoscience
B. Metallo-Enzymes & Metal Chelators
C. Interfacial Science, Corrosion & Separations
D. Catalysis/Biocatalysis
E. Alternative Solvents
F. Waste Treatment
G. Supporting Capabilities & Technologies

The body of this report provides examples of the Technological Challenges and Enabling Research Areas relevant to energy and the environment. The report concludes with a description of an effective approach to research support in these areas.

Challenges in Energy and Environmental Science

This section outlines some of the opportunities for chemists, either as individuals or as part of an interdisciplinary team, to address the technological challenges associated with energy and environmental problems.

1. Energy:

Energy utilization, irrespective of the energy source, has environmental consequences. The environmental impact of energy production and utilization ranges from the release of greenhouse gases (e.g., CO_2, N_2O) and air pollutants (e.g., SOx, NOx, and hydrocarbons) produced from combustion to land use associated with alternative sources of energy, such as biofuels or solar energy. Nuclear energy raises environmental concerns about long term storage of radioactive waste. An understanding of these consequences and how to deal with them requires a knowledge of the relevant fundamental molecular chemistry.

Challenges:

- Nuclear Power (Waste Disposal, Radiation Health Effects, Soil & Atmosphere Contamination)
- Manufacturing Efficiency (Energy Use, Water, Air & Soil Pollution)
- Alternative Fuels (Higher Hydrogen Content)
- Clean Energy (Photovoltaic, Photocatalytic Energy and Fuel Production, Fuel Cells, Hydro-, Wind-, Geothermal-Power)
- Oil Recovery Efficiency (Energy Reserves, Energy Costs)
- Production of CO_2 and Other Greenhouse Gases (Global Change)
- Small Particle Emissions (Human Health)

2. Chemical Synthesis & Processing:

The chemical industry is a major sector of the United States economy generating more than $250 billion in sales with a trade surplus >$15 billion. It is relatively efficient with average overall yields of basic chemicals >90%. However, the chemical industry still produces more than 10.5 billion tons of hazardous and non-hazardous waste annually. Most of the chemical waste is in the form of dilute aqueous streams. An estimate of the mass of chemical by-products in waste water is 0.1 billion tons. This is an enormous quantity, ~50% of the total annual generation of municipal solid waste. Roughly 80-90% of the hazardous waste generated comes from chemical manufacturing. Improvements in the efficiency and selectivity of chemical processes are required to significantly reduce environmental pollution.

Challenges:

- One-operation sequences to target compounds
- Biocatalysis coupled to catalysis, electrochemistry, or photochemistry
- Waste Minimization and Recycling
- Energy Efficiency
- Alternative Feedstocks
- Alternative Solvents

Clean Air:

Energy consumption can have significant effects on air quality and related human health and environmental concerns such as global change, stratospheric ozone depletion, smog and airborne particulate matter. Research is required to understand the relationship between energy related activities and these air quality concerns. Research would include, for example

- Studies of sources and subsequent processing of gas and condensed phase materials in the atmosphere.
- Research on the formation, composition, thermodynamic properties, and surface reactions of aerosols
- Research leading to reduced undesirable emissions from automobiles and other energy utilization sources

Challenges:

- Airborne Matter (Particulate Matter ≤ 2.5 microns, Ultrafines, Dust, Cloud Condensation Nuclei, Other Aerosols, Sea Salt, Soot, etc.)
- Smog (Ozone, Organics, NOx, Other Inorganics)
- Global Change Gases (CO_2, N_2O, NH_3, …)
- Indoor Environments
- Stratospheric Ozone

4. Clean Water:

Chemical research is linked to the challenge of clean water at three levels: i) eliminating the release of chemical pollutants; ii) elucidating the fate of chemical pollutants in the natural environment; and iii) understanding the natural compounds and processes in aquatic systems. Almost all chemical pollution is tied to the energy, manufacturing, mining, and agricultural industries. Improvements in the design of chemical products, in manufacturing processes, and in agricultural practices are key to the maintenance of water quality. The fate, transformation and bioavailability of chemical pollutants are largely controlled by chemical processes. The identification of natural compounds and processes (e.g., so-called humic materials and their transformations) is also fundamentally a chemical problem.

Challenges:

- Pesticides & Fertilizers (Eutrification, Nitrates in Ground Water)
- Humics & Fulvics
- Colloids
- "Chlorine Byproducts" (harmless *vs* carcinogenic)
- Microbes
- Solvents & Water Utilization
- Heavy and/or Reactive Metals

5. Clean Earth:

Chemical and biological processes at complex environmental interfaces play a major role in controlling the mobility, toxicity, potential bioavailability, and ultimate fate of environmental contaminants in the biosphere. For example, heavy metal ions in groundwater, such as As(III), Se(VI), and Hg(II), can be transformed into more or less toxic forms by chemical reactions that may occur at the interfaces between aqueous solutions and mineral surfaces, biofilms, or humic materials. Many such transformations occur in the environment, yet there is little understanding of these processes at a molecular-mechanistic level. Environmental interfaces and the processes occurring at these interfaces are extremely complex, and the concentration levels of contaminants are very low. Understanding at the molecular level including development of new nanoscale probes, such as extremely sensitive element-specific spectroscopies, requires a multidisciplinary effort by chemists, geochemists, engineers, and modelers.

Challenges:

- Biogeochemical Cycling on a Global Scale (Carbon, Nitrogen, Trace Elements, etc.)
- Soil Contamination
- Transformations (Field or Regional Scale)
- Exchanging Chemicals with Air and Water (e.g., Hg)
- Reactive Transport

Enabling Research Areas in Energy and Environmental Sciences

Opportunities abound for major advances in energy and environmental sciences through the understanding and development of solutions at the molecular level. This section provides some examples where molecular level science could have an important impact.

A. Materials Synthesis and Nanoscience

The ability to synthesize porous solid materials with control over the size, structure, and chemical functionality would lead to tremendous advancements in such technologies as shape selective catalysis or high performance separations. New methods for materials assembly need to be developed. For example, the synthesis of molecular sieves with enhanced hydrothermal stability, based on new compositions, would open many new applications. The synthesis of solid surfaces with high densities of specific atomic structural arrangements would make possible highly selective adsorbants that could be applied to solve problems in chemical separations or chemical sensing.

The ability to rapidly characterize new materials will facilitate the efficient exploration of synthetic approaches. Fundamental studies of the chemical and electronic properties through a series of systematically structured materials would provide a basis for establishing a theory of structure-property relationships. Understanding the role of earth materials with particle sizes in the nanometer range in natural systems is also an increasing need. Studies of complex natural systems at a level of detail similar to laboratory investigations are necessary. Because of the complexity of these systems, particularly those involving organic matter and microbial processes, multidisciplinary approaches are essential.

B. Metallo-Enzymes and Metal Chelators

The study of natural metalloenzymes and metal chelators is a significant research opportunity for chemists in environmental sciences. The unusual conditions under which enzymes must function in nature (e.g., very low or very high metal concentrations or extremes of temperature) suggest that the metal centers in such enzymes are often quite different from those studied in model systems. Similarly, intracellular and extracellular chelating agents exist in nature—some with extreme affinity and specificity for a particular metal—which are yet uncharacterized.

A knowledge of the structure and properties of natural metalloenzymes and chelators is important for understanding key steps in the global cycle of elements such as carbon and nitrogen. Such enzymes and chelators may also prove useful in waste treatment, pollution remediation or manufacturing.

C. Interfacial Science, Separations, and Corrosion

Reactions at natural interfaces among minerals, aqueous solutions, and gases determine, in large part, the composition of the earth's near-surface environment. New types of chemical separations methods based on interfacial reactions could control the composition of waste streams in chemical manufacturing and eliminate processing by energy intensive distillation or sorption. The design of strong and durable materials capable of withstanding the rigors of stress and weathering over long periods of time would alleviate costly losses particularly in the construction and transportation industries. An understanding of the chemical and biological processes that control interfacial chemistry is essentially lacking at the molecular level. This limits our ability to understand complex interfacial processes in the natural environment and to design interfaces that are part of engineered systems.

D. Catalysis/Biocatalysis

Catalytic chemistry is essential in chemical and biological processes. Highly selective catalysts would make cleaner, one-step industrial chemistry a reality. Catalysts that give durable, low temperature activity—down to room temperature—are needed in mobile and decentralized locations. Catalytic systems with high temperature durability are also needed in combustion, automotive exhaust and fuel cell reforming. Biocatalytic routes to chemicals and fuels will enhance sustainability and carbon balance. Both recombinant organisms in whole-cell fermentations and plasmid engineered microbes can effectively be used to either metabolize certain chemicals to useful building blocks or to synthesize defined value-added products from renewable resources.

E. Alternative Solvents

Over 30 billion pounds of organic and halogenated solvents are used world-wide each year. The amount of water used and contaminated is much larger. The development of alternatives to organic- and water-based solvents could significantly reduce air and water pollution. Using solvents with a low heat of vaporization, such as supercritical CO_2, would substantially improve the energy efficiency of cleaning and chemical synthesis. For example, drying PVC made in water requires 1 trillion BTUs/ year.

F. Waste Treatment

Any chemical waste generated by large scale manufacturing should be subjected to disposal through a strategic conversion to other products that have a defined use rather than destruction by either incineration or soil digestion. The common sense approach calls for microbiologists and synthetic chemists to collaborate in exploring the potential of organic waste as a feed stock for providing fine chemicals to pharmaceutical sector for further use.

G. Supporting Capabilities and Technologies

A molecular level understanding of the chemistry of complex systems will play an important role in the success of the enabling research programs listed above. New methods of measurement, advances in theoretical methods and database improvements are critical to achieving this understanding.

Measurement Science: Measurement strategies are needed which operate in complex environments and provide local compositions on a molecular length scale for time scales from a few femtoseconds to much longer times. Recent progress in physical chemistry has lead to remarkable new probes that have a high potential to yield such information.

Simulation Technology: Modeling and Simulation are essential tools in studies of complex systems where understanding cannot be definitively determined through characterization alone. For low density systems present theory can lead to semiquantitative predictions for energetics and reaction rates. For problems in which condensed phases are involved, new theoretical developments are required. The dynamics in these systems typically involve the simultaneous interaction of many particles and important time scales may vary from femtoseconds to the macroscopic time scales of equilibrium behavior. Both quantitative and conceptual models are required. Experimental validation will be a key component in the evaluation of the approximations inherent in theories of complex materials and processes.

Database Development: Reaction rates, mechanisms, thermodynamics and structures are often unknown for the complex systems and materials related to energy utilization and its environmental impacts. The considerable body of existing thermodynamic, phase stability and kinetic data is limited, for the most part, to one or two component systems near standard temperature and pressure. In many relevant systems there is a great need for expanded thermodynamic databases and accurate phenomenological models that can be parameterized from limited data. A microbial transformation database is also needed that matches known pollutants with known biodegrading organisms. For multi-disciplinary work on national issues it is important that databases containing such information be made widely available to the research community.

Research Support

NSF and DOE could develop strategies to encourage researchers who are not currently doing energy- and environmentally-related research to move into this emerging area and could also provide significant support to help individuals and collaborative groups on a longer-range continuing basis. One possibility is to heighten awareness of research opportunities for linking basic science with potential solutions to environmental problems. Enabling researchers to explore extensions of their current research to new problems of societal significance and to establish new collaborative efforts would also be important.

A multi-faceted approach that includes concepts for both **Initiation Activities** and **Ongoing Support** was evaluated and supported by workshop participants.

A. Initiation Activities

1. Exploratory grants/supplements:

Researchers could explore new areas of environmental interest with modest levels of funding (ca. $50,000/year) for 2 years. Initial results providing "proof of concept" would allow a more complete, competitive proposal to be developed. These grants might take the form of exploratory grants or supplements to ongoing NSF/DOE grants.

2. Personnel Exchanges:

Energy and environmental chemistry are inherently multidisciplinary. Awareness of the important issues often requires interacting with other researchers in the field as well as researchers from other fields. Small grants and contracts that serve to link academics with personnel in national labs or industrial sites can foster the interactions required for multidisciplinary science. Models for this kind of support are the GOALI proposals currently funded by NSF or the PAIR program funded by DOE. Unfortunately, as presently constituted, these do not include the national labs or emphasize energy and environmental research

3. Workshops:

Workshops promote communication between academics and national laboratory or industrial scientists that may develop into formal collaborative activities.

4. Training grants:

Collaborative research is strengthened when students and post-docs serve as the link between different researchers. Support of "training grants" targeted to this initiative would enhance research opportunities for students interested in energy and environmental chemistry.

B. Ongoing Support

Research in energy and environmental chemistry can be sufficiently broad and complex to require interdisciplinary teams of faculty with diverse interests and expertise. However, many problems are better studied by individual investigators working in their own laboratories. Opportunities for both types of research are needed, but interdisciplinary partnerships need to be encouraged. Major initiatives involving collaborative groups would catch the attention of the research community and inspire participation. Two types can be envisioned:

1. Collaborative Research Groups in Energy and Environmental Chemistry (CRGs):

Teams of 2-5 researchers would receive funding in the neighborhood of $300k-500k /year. The Focused Research Groups sponsored by the NSF Division of Materials Research could serve as a model. Teams may consist entirely of university personnel, but the research may benefit substantially from active collaboration with national laboratory personnel and their facilities, and/or collaborations with industry. This kind of collaboration could be subjected to a peer review after ca. 5 years, to evaluate progress, with the possibility of a competitive renewal.

2. Molecular Energy and Environmental Science Centers (MEESCs):

Larger teams of faculty (>7) could be supported to target broader areas of importance to energy and environmental research or especially complex problems. An appropriate mechanism for these larger teams might be the establishment of centers. Centers should have substantial education and outreach components in addition to the research. Funding up to $2 Million /year for 5 years is appropriate and could include a significant component of instrumentation resources and infrastructure support as part of their operating budget. As with the smaller collaborations, a 5 year review cycle would be an appropriate evaluation mechanism.

C. Level of Support

The National Science Foundation and the Department of Energy could take advantage of new opportunities in experimental and theoretical methods by launching major initiatives in energy and environmental chemistry. The complexity and breadth of the Technological Challenges and Enabling Research Areas warrant a substantial investment. Using the models described above as examples, it would be appropriate to invest in approximately 7 MEESC's, each funded at a steady-state level of $2 Million /year, and 40 CRG's, each funded at $300k-500k per year to meet the scientific opportunities. About 5-10% of the effort would be appropriate for initiation activities. Funding of this magnitude would yield significant improvements in our understanding of energy and environmental science at the molecular level and would provide a highly visible indication of the commitment by NSF and DOE to solving energy and environmental problems.