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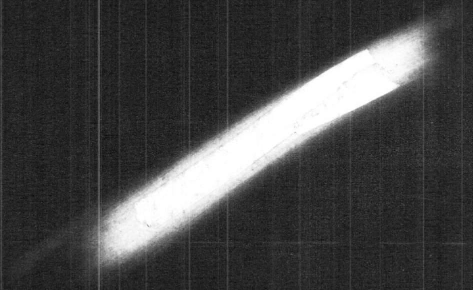

Summaries of FY 1985 Research in the Chemical Sciences

September 1985

U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences

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This report was compiled for the Office of Energy Research project from summaries contained in the Research-In-Progress (RIP) data base of the Office of Scientific and Technical Information, Oak Ridge, Tennessee. The RIP data base describes new and ongoing energy and energy-related research projects carried out or sponsored by the Department of Energy.

PREFACE

The purpose of this publication is to inform those interested in research supported by the Department of Energy's Division of Chemical Sciences, which is one of six Divisions of the Office of Basic Energy Sciences in the Office of Energy Research. This publication includes projects supported by both the Chemical Sciences budget and that portion of the Nuclear Sciences budget which is administered by the Division of Chemical Sciences.

These summaries provide to members of the scientific and technical public and interested persons in the legislative and executive branches of the Government a means for becoming acquainted, either generally or in some depth, with the Chemical Sciences program. Areas of research supported by the Division are to be seen in the section headings, the listing of "Selected Topics of General Interest," and the summaries themselves. Energy technologies that can be advanced by use of the basic knowledge generated in this program are provided in the "Selected Topics" list and also (by reference) in the summaries.

Chemists, physicists, chemical engineers, and others who are considering the possibility of proposing research for support by this Division will find the publication useful for gauging the scope of the present program in basic research and the relationship of their interests to the overall program. Proposals that expand this scope will also be considered or directed to more appropriate offices. The research summarized here is intended to add significantly to the knowledge base on which successful energy technologies can grow. For this purpose, scientific excellence is a major criterion applied in the selection of research supported by the Division of Chemical Sciences. Another important consideration is the emphasizing of chemical, physical, and chemical engineering subdisciplines which are advancing in ways that produce new information related to energy, needed energy data, or new ideas.

The program is distributed among several different kinds of performing organizations. About half the projects take place at DOE laboratories, and half take place at universities and industrial laboratories. In DOE laboratories, most of the researchers are fully engaged in this work, while most university and industrial researchers necessarily divide their time among duties involving this research, other research, teaching responsibilities, etc.

Questions about the details of an individual project may be directed to the investigators involved or the persons in charge at DOE Laboratories (who are identified at appropriate places in this publication). Other questions about the program may be directed to the undersigned.

Elliot S. Pierce, Director
Division of Chemical Sciences
Office of Basic Energy Sciences

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*On detail from the National Bureau of Standards.

†On leave from Seton Hall University.

Each Branch of the Division of Chemical Sciences is divided into programs which cover various disciplines. The following summaries describe these programs. The staff members responsible for each program are indicated on page ii.

Fundamental Interactions Branch (KC-03-01-)

Photochemical and Radiation Sciences (KC-03-01-01)

The Photochemical and Radiation Sciences program consists of research into the interactions of radiation with matter in all forms but particularly with gases and liquids. The photochemical research is devoted largely to studies with visible radiation aimed at the capture and conversion of solar energy. This encompasses such fields as artificial photosynthesis, photoinduced electron transfer reactions in homogeneous and heterogeneous media, photoelectrochemistry, and photocatalysis. The radiation chemistry research is concerned with the chemical effects produced by absorption of energy from ionizing radiation. A small part of the program is devoted to research in hot atom chemistry, i.e., the study of the effects of nuclear decay and the consequent release of energy on chemical reactions. A new and growing program of photochemistry, spectroscopy, and related studies is centered at the National Synchrotron Light Source at Brookhaven National Laboratory.

Chemical Physics (KC-03-01-02)

The Chemical Physics program supports research in a diverse set of disciplines with a goal of providing basic knowledge in areas related in the nation's energy needs. A significant portion of the program is in the many-faceted area of chemical kinetics, including energy transfer, chemical dynamics involving state-selected chemistry, unimolecular and bimolecular research kinetics, as well as the reactions of clusters. Research efforts in molecular structure, spectroscopy, and theoretical chemistry are also well represented in this program.

Special emphasis is placed on basic research related to combustion; advanced diagnostic methods, spectroscopy, theory, and the kinetics of elementary combustion reactions are of special interest. A major user-oriented facility, the Combustion Research Facility (CRF) at Sandia Laboratories/Livermore is supported by this program. This laboratory offers use of advanced instrumentation to interested combustion scientists from universities, industry, and national laboratories.

Atomic Physics (KC-03-01-03)

The Atomic Physics program supports experimental and theoretical efforts associated with the study of atom and ion structures, energy levels and lifetimes of quantum states, and of transport and exchange processes characterizing transfer of energy, momentum, and matter. These studies strive to obtain the best and most complete fundamental knowledge of the properties and interactions of photons, electrons, atoms, ions, and simple molecules. Continued emphasis of this research has been on the understanding of relatively high energy atomic physics that involves atoms stripped of all or most all electrons and of atoms and ions in which electrons are located at upper energy levels. The study of processes that lead to the production of coherent radiation and of the statistical properties of this radiation as they modify elementary atomic physics processes also constitute part of this program.

Processes and Techniques Branch (KC-03-02-)

Chemical Energy (KC-03-02-01)

This program includes basic chemistry research related to chemical transformations or conversions which are fundamental to new or existing concepts of energy production and storage. Of particular interest are those research activities with the objectives of understanding the chemical aspects of (1) catalysis, both heterogeneous and homogeneous, (2) the chemistry of fossil resources, particularly coal, including characterization and transformation, and (3) the conversion of biomass and related cellulosic wastes. The disciplines of organic, bio-, inorganic, physical, thermo-, and electrochemistry are central to this program. The emphasis is on understanding the chemical principles underlying the new and developing technologies and on innovative chemical research with potential for new energy concepts.

Separations and Analysis (KC-03-02-02)

The separations part of the program is directed toward improving our basic understanding of methods for separating mixtures of gases, liquids, solids, and their component molecules, cations, anions, and isotopes. The program covers a broad spectrum of separations concepts, including membrane processes, extraction at both standard and supercritical conditions, adsorption, chromatography, photodissociation, complexation, etc. The program is technique oriented rather than species oriented; i.e., the research involves elucidating fundamental chemical phenomena for improved separations rather than developing specific processes for the separation of a particular species from particular matrices. The isotope separation program emphasizes isotopic properties and isotope effects and is basic in nature.

The analysis part of the program is aimed at supporting research on analytical techniques where a better understanding of basic chemical phenomena may facilitate improvements in sensitivity, reliability, and ease of operation and/or lower the costs of analytical determinations. Entirely new analytical techniques are also investigated, although this program does not support instrument development. New techniques are quickly reported in the literature so that those interested in instrument development can build on work supported herein. The program is not geared to using existing techniques to unravel the composition of samples nor to developing techniques to analyze particular chemical species or sample types. Rather, it is aimed at obtaining a thorough understanding of the basic chemistry of an analytical technique so that others may use this understanding to improve its utility.

Chemical Engineering Sciences (KC-03-02-04)

This program addresses the more specific and energy-related aspects of chemically related engineering topics, including thermodynamics and physical and chemical rate processes. Particular attention is given to turbulence research related to combustion, experimental and theoretical thermochemical and thermophysical properties, and phase equilibria, especially of mixtures, including supercritical phenomena. Emphasis is given to improving and/or developing the scientific base for engineering generalizations and their unifying theories.

Isotope Preparations (KC-01-02)

The Isotope Preparations program is dedicated to the production of research quantities of isotopically enriched research materials by way of the Electromagnetic Isotope Separations (Calutron) facility, the High Flux Isotope Reactor (HFIR), and the Transplutonium Processing Plant (TRU). These facilities are described on pages ~~93 and 94~~ of this book. These research materials are made available to an international user community from a sales inventory, by loan from a Research Materials Collection, and by cost-free allocation from the DOE Research Materials/Transplutonium Program Committee.

94&95

Heavy Element Chemistry (KC-01-02-03)

The Heavy Element Chemistry program focuses on a study of the chemical and certain physical properties of the actinide elements, principally the transuranium elements, because of the importance of these elements to DOE's nuclear programs and to an understanding of the basic science in general. A variety of investigations are pursued, including (1) organometallic chemistry, (2) the chemistry of excited spectroscopic states, (3) thermochemistry of actinides in complex oxides and binary halides, (4) the chemistry of actinides in near-neutral aqueous solutions and the reactions of aqueous actinides ions with various complexing agents, (5) the development of preparative methods for actinide metals and compounds, and (6) the measurement of crystal structures, melting points, magnetic susceptibilities and the behavior of actinide metals under pressure. This research is performed principally at the National Laboratories because of facilities required for handling radioactivity.

Chemical Sciences Division

Stanford Synchrotron Radiation Laboratory (KC-01-03)

Support for the operation of the Stanford Synchrotron Radiation Laboratory (SSRL) is provided through this category. Access to this facility is possible by the submission of individual proposals directly to SSRL and successful outcome through a peer review process conducted by SSRL's program committee, a representative group selected by users of the facility. The research carried out by the users represents a broad field of disciplines not confined to those supported by the other categories listed above. As a consequence, most of the research projects using SSRL are funded by other DOE offices, other agencies and private sources.

LABORATORY ADMINISTRATION

Listed below, by laboratory and department or division, are persons who are in charge of the Division of Chemical Sciences projects at DOE laboratories. These individuals are laboratory, department, or division administrators who can provide information about specific programs or refer inquiries to appropriate individuals.

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Chemical Physics

Atomic Physics

Chemical Energy

Separation and Analysis

Chemical Engineering Sciences

Heavy Element Chemistry

Stanford Synchrotron Radiation Laboratory Operation

SUMMARIES OF FY 1985 RESEARCH IN THE CHEMICAL SCIENCES

NATIONAL LABORATORIES

Photochemical and Radiation Sciences

Ames Laboratory
Ames, Iowa 50011

Fundamental Interactions Program **$290,000**

1. *Laser Spectroscopy and Electronic Energy Transfer of Light Conversion Systems*
G.J. Small

This project centers on (1) the structural organization and intermolecular interactions of pigments in artificial and naturally occurring photosynthetic aggregates and (2) the use of efficient electronic energy transport in biomimetic chromophoric polymers in solar energy conversion. A variety of laser spectroscopies are used (e.g., optical hole burning, fluorescence line narrowing, picosecond spectroscopy). Very facile nonphotochemical hole burning has recently been observed for both chlorophyll a and b monomers in polystyrene polymer films. It will now be possible to employ hole burning to study (in a very precise way) the intermolecular interactions that dictate dimer formation of photosynthetic pigments. Such formation is important for the photosynthetic apparatus. Ultimately, hole burning will be used as a diagnostic tool for studying dimers in actual reaction centers. In addition, nonlinear laser spectroscopies are used to study coherent unidirectional energy transfer and the vibrational structure of molecular solids. The approach is unique and will reveal (for the first time) the mechanism associated with the final step in donor to acceptor (trap) electronic energy transfer. [3.0 FTE]

2. *Picosecond Spectroscopy and Reaction Dynamics*
W.S. Struve

Picosecond fluorescence spectroscopy is used to study excited state decay processes of dye molecules adsorbed on semiconductors and insulators. Since an accurate theory has not yet been developed for excitation transport and trapping in two dimensions (i.e., on surfaces), we have been obtaining detailed fluorescence profiles for well-characterized dye and excitation trap coverages on fused quartz to assess the limitations of the present theory. We have also examined fluorescence decays of dyes adsorbed on semiconductors, and have found that dye-to-surface mode nonradiative decay is an extremely fast process on TiO_2 and ZnO. The importance of this decay mode has been recognized earlier for dyes on metals, but it appears that its rate is similarly fast on semiconductors. We have shown that dye-to-surface mode nonradiative decay is the dominant decay mode for dyes on TiO_2 at dye-surface separations between ~ 100 and 500 Å. An extrapolation of the theoretical separation-dependent decay rate constant (which fits our data) shows that this decay process is a subpicosecond process for separations < 2 Å. Thus, it is a likely origin of low photocurrent yields in liquid junction cells. [2.5 FTE]

Argonne National Laboratory
Argonne, Illinois 60439

Chemistry Division **$4,360,000**

3. *Preparation of Organisms, Photosynthetic Pigments, and Biological Materials of Unusual Isotopic Composition*
H.L. Crespi, J.J. Katz, J.R. Norris, M. Wasielewski

The project objective is the production of photosynthetic microorganisms substituted with biologically important stable isotopes. The major effort is in the production of fully deuterated organisms, but the Argonne National Laboratory Chemistry Division is able to grow organisms in which nonmagnetic ^{12}C is replaced by magnetic ^{13}C, ^{14}N by ^{15}N, ^{16}O by ^{17}O or ^{18}O, and ^{24}Mg by ^{25}Mg. Large quantities of green algae, blue-green algae, and photosynthetic bacteria are routinely available in unnatural isotopic composition involving either single or multiple substitution. These organisms (and the compounds obtainable from them) have important applications in magnetic resonance spectroscopies, small-angle neutron scattering, and resonance Raman spectroscopy. Typical areas of interest are applications in the study of chlorophyll, photosynthesis, biomimetic photochemistry, and bacterial photosynthetic reaction centers. Of particular importance is the ability to provide material for the growth of single crystals containing unusual isotopes. Genetically engineered bacteria are also cultured to give good yields of the protein of interest. [1.0 FTE]

4. *Gas-Phase Radiation Chemistry and Photochemistry*
C.D. Jonah, D.B. Bartels, A.D. Trifunac, D.B. McDonald, M.C. Sauer, Jr.

This project measures rate constants for simple free radical reactions, of great importance in atmospheric and combustion chemistry. The pulse radiolysis technique makes it possible to measure the kinetics at pressures of 1 atm and above and over the temperature range of 50 to 1000°C, a range no other single experimental technique can easily span. The reaction rates of OH and OD radicals with CO and simple radicals are under investigation as well as the rate of production of hydrogen atoms from the reaction OH + CO. In addition to the practical importance of these reactions to combustion, the data serve as an excellent test for reaction theories because of the rigorous restrictions provided by the wide temperature range and the use of two hydrogen isotopes. [3.5 FTE]

5. *Chlorophyll and Photosynthesis Research*
J.J. Katz, J.C. Hindman

The principal objective of this research is to acquire sufficient knowledge about chlorophyll function in natural photosynthesis to ultimately make possible the replication of the natural primary light conversion event outside the living cell. Current focus is on: (1) laser photochemistry and photophysics of chlorophyll and chlorophyll model systems; (2) new methods for the synthesis of chlorophyll and bacteriochlorophyll model systems; (3) characterization of a new chlorophyll from a recently discovered photosynthetic bacterium, *Heliobacterium chlorum;* (4) applications of ^{252}Cf plasma desorption mass spectroscopy and high performance liquid chromatography to chlorophyll compounds and model systems; (5) structural studies by small angle neutron scattering of chlorophyll aggregates and natural photoreaction centers; and (6) re-examination of enhancement in oxygen evolution in green plants. [3.8 FTE]

6. *Electron Transfer and Energy Conversion and Storage*
J.R. Miller, D. Meisel, K.H. Schmidt, M.C. Thurnauer

This project aims at (1) the fundamental understanding of electron transfer between molecules held apart at fixed distances and (2) the study of chemical mechanisms involved in the conversion and storage of light energy. Electron transfer rates are measured by pulse radiolysis of solids or compounds containing two functional groups separated by rigid molecular spacers to determine the effects of distance, energy, and molecular structure. The work on energy conversion and storage utilizes various microenvironments (1) to enhance charge separation and thus the efficiency of photoelectron transfer and (2) to increase the yield of photo-redox products while minimizing the rates of back reactions. Particular attention is given to mechanistic studies of catalytic water-splitting in colloidal systems and in microenvironments such as micelles, polyelectrolytes, and membranes. [7.6 FTE]

7. *Physicochemical Investigation of Photosynthesis*
J.R. Norris, M. Wasielewski, M. Bowman

The project objective is to elucidate the molecular mechanisms whereby light energy is converted into chemical charge separation. Natural photoreaction centers are investigated in detail so that efficient model systems can be constructed. Emphasis is on determining the structural arrangement during the natural photosynthetic charge separation process for duplication in artifical photosynthesis. Time-domain spectroscopy is used to measure distances, orientations, and dynamics within the molecular components that participate in the transfer of electrons. Electron transfer events that occur in the range of a few picoseconds and longer are probed by optical and magnetic techniques. Magnetic methods and theory are developed specifically to characterize picosecond charge separation in chemical systems. Charge separation in single crystals of the reaction centers of several photosynthetic bacteria is investigated by magnetic and optical spectroscopy as well as x-ray and neutron diffraction. [4.8 FTE]

8. *Radiation Chemistry and Photochemistry in Condensed Phases*
A.D. Trifunac, C.D. Jonah, M.C. Sauer, Jr., D.B. Bartels, D.B. McDonald

The project objective is the study of chemical and physical processes following ionization (or photoionization) in both polar and nonpolar liquids. This is relevant to understand breakdown in dielectric liquids and to understand charge separation, recombination, and transfer phenomena, which are the basis of chemical and biological processes of energy storage and use. Various methods of radiation chemistry and photochemistry are used to provide details of the nature and dynamics of the early transient species and their chemical fates. This includes the study of electrons and positive ions, radical ions and excited states, and the subsequent fragmentation of the excited species into radicals and molecular species. Photochemistry and spin dynamics in radicals and radical ions are being examined to provide better understanding of reaction mechanism. Pulse radiolysis is used to study redox reactions of actinides and lanthanides. Essential tools used in this project are the Argonne high-current picosecond electron linac, the pulsed Van de Graaff accelerator, and innovative, time-resolved, magnetic resonance and laser techniques, which are being developed and applied to these problems. [15.6 FTE]

9. *Artificial Photosynthesis*
M. Wasielewski, J.R. Norris

The goal of artificial photosynthesis research is the development of molecular systems in the laboratory that not only mimic but improve upon natural photosynthetic energy conversion. This work focuses on several interrelated facets of this problem. First, a molecular design project involves the synthesis of molecular models of the natural energy conversion system. These models, through their mimicry of features of natural photosynthesis, aid in the structural and mechanistic understanding of the natural process. Second, the photophysics and photochemistry of these systems are studied with emphasis on light-induced electron transfer reactions. Advanced spectroscopic techniques such as picosecond spectroscopy and time-domain magnetic resonance are used to study these ultrafast processes. Third, the primary photosynthetic processes themselves are being investigated with a view toward integrating the information obtained from the laboratory systems with new knowledge of natural photosynthesis. [3.2 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Applied Science Department $1,155,000

10. Porphyrin Chemistry
J. Fajer

This project focuses on (1) the function of chlorophylls in the photosynthetic transduction of light into chemical energy, (2) the catalytic role of porphyrins in bioenergetic enzymic reactions, and (3) the application of these reactions to synthetic multi-electron photocatalysts for the fixation of carbon and nitrogen and the decomposition of water. Work in synthetic, structural, physical, and theoretical chemistry includes: (1) storage of oxidizing equivalents in photosystem II and the nature of primary electron donors in green plants; (2) conversion of carbon dioxide to methane by corphins; (3) six-electron reduction of nitrite to ammonia mediated by isobacteriochlorins; (4) light harvesting in photosynthetic bacteria; (5) theoretical and experimental modeling of environmental effects on the properties of porphyrins, chlorophylls, and their radicals; (6) x-ray diffraction of chlorin, chlorophyll, and isobacteriochlorin derivatives as models of *in vivo* architecture; and (7) picosecond electron transfers in reaction centers and in covalently-linked porphyrins modeled on the mechanisms postulated for photosynthetic organisms. [7.9 FTE]

11. Electrochemistry and Photoelectrochemistry
S. Feldberg, T. Skotheim

The project objective is the understanding of a variety of electrochemical and photoelectrochemical phenomena. Theoretical studies comprise (1) analysis of square-wave and sine-wave perturbations in semi-finite diffusion; (2) analysis of the effect of picosecond irradiations of semiconductor systems (elucidation of factors affecting bulk and surface electron-hole recombination); (3) analysis of an unusual electro-catalytic system; and (4) simulation of the rotating ring disc electrode. Experimental studies include (1) investigations of photoelectro-chemical cells using junctions between polypyrrole-coated semiconductors and poly-(ethylene oxide) doped with KI/I_2, a solvent-free solid polymer electrolyte; (2) investigations of the use of doped poly-(ethylene oxide) in electrochemical cells compatible with the ultra high vacuum required by spectroscopic techniques (e.g., ESCA, SEXAFS, and NEXAFS,); (3) investigation of the spectroelectrochemistry of polypyrrole to elucidate the mechanism of electrochemical switching; and (4) characterization of (oxidized) polypyrrole stabilized with a sulfonated metallophthalocyanine counterion. [3.5 FTE]

12. Chemical Properties and Reactions of Mono- and Dinuclear Ferrocene Derivatives
M. Hillman

This project investigates the preparation and properties of metallocenes and related compounds expected to have application in the energy program, especially toward the splitting of water. For the oxidation of water, ferrocene derivatives with potentials high enough to oxidize water under neutral or slightly acid conditions are required. Preparation of compounds with these properties are underway. For the reduction of water, the mechanics of the generation of hydrogen from [1.1] ferrocenophanes with strong acids are studied. Rates for hydrogen formation have been determined for three ferrocenophanes. These results indicate that the orientation of the protons on the iron atoms is a significant condition for the reaction. An understanding of this reaction will enable further modifications of the ferrocenophane so that hydrogen may be obtainable from weak acids, perhaps even water. [3.5 FTE]

Chemistry Department $2,725,000

13. Radiation Chemistry
B.H.J. Bielski, R.A. Holroyd, H.A. Schwarz

This project uses pulse radiolysis and photolysis to study the behavior of transient chemical species. Principal areas of investigation are: (1) properties and reactions of electrons in dielectric fluids; (2) photoionization in dielectric fluids; (3) formation and reactions of transition metal ion complexes in unusual oxidation states; (4) the nature of transition metal ion-hydroperoxyl radical complexes; and (5) other reactions of the hydroperoxyl radical. An understanding of electrons in dielectric fluids is of prime importance in explaining the basic processes of radiation chemistry, in the development of new detectors for high energy physics and EXAFS measurements, and in controlling dielectric breakdown in transformers. The studies of transition metal complexes and hydroperoxyl radical reactions are important in developing and understanding certain homogeneous catalysis systems and methods of chemical storage of solar energy. [8.7 FTE]

14. Photochemical Energy Conversion and Solution Kinetics
N. Sutin, C. Creutz, T.L. Netzel,
B.S. Brunschwig

Because they strongly absorb visible light and readily undergo electron-transfer reactions, transition metal complexes are excellent mediators of outer-sphere, light-induced redox reactions, many of which affect net storage of the light energy. In addition, because of their ability to promote the formation or activation of small molecules, transition metal complexes can provide homogeneous catalytic routes for the thermal and photochemical formation of H_2 or activation of CO_2. This project encompasses fundamental studies of the reactions of excited-state and ground-state complexes. Since efficient light conversion and storage require the diversion of a significant fraction of the electronically excited molecules into useful reactions, which must be driven in competition with rapid physical deactivation processes (luminescence and radiationless decay) and chemical back-reactions, a major objective is the quantitative study and control of these physical and chemical deactivation processes. The lifetimes of excited states and the rates of electron-transfer reactions of excited-state and ground-state complexes are being determined and modeled. Because the overall efficiency of the conversion sequence is determined by the nature and rate of the subsequent chemical steps, mechanistic studies of the reaction of transition metal ions in high and low oxidation states are also being conducted. [11.1 FTE]

15. Energy Transfer in Chemical Kinetics
R.E. Weston, J.M. Preses

The distribution of reactant energy among translational, rotational, vibrational, and electronic degrees of freedom is a major factor in determining chemical reaction rates. Conversely, the energy distribution in reaction products provides a sensitive probe of the reaction dynamics. Collisional energy transfer plays an important role in the reaction mechanism as a process by which energetic species are produced or removed. This project studies the transfer of translational, vibrational, or electronic energy. Atoms or molecules are produced in excited states by a pulse of ultraviolet, visible, or infrared radiation. The time-dependent disappearance of these excited species is monitored by the detection of radiation, either from the parent species or from molecules that have been excited by collisional energy transfer. This project also supports both in-house research and assistance to outside users at the Dynamic Spectroscopy Beamline on the vacuum ultraviolet ring of the National Synchrotron Light Source. [5.8 FTE]

16. *Chemical Dynamics of Stable and Transient Species in the Gas Phase and on Surfaces*

A.P. Wolf, R.A. Ferrieri

The overall goal of this project is to further our understanding of the chemical dynamics for reactions that are important to energy production processes. Immediate focus is to evaluate the mechanistic and kinetic aspects of state-selective reactions of excited carbon, nitrogen, and oxygen atoms with stable molecules in the gas-phase using moderated nuclear recoil (hot atom) and accelerated ion techniques. Similar aspects of the chemistry of other important intermediates (e.g., NH_x, NO_x, and CN) will also be investigated. We will investigate the kinetic aspects of surface catalyzed reactions using short-lived positron emitting radionuclides as transient probes that enable rapid kinetic measurements to be made with ultra-sensitive surface detection. Of importance is understanding of the state-selectivity that controls specific chain-growth mechanisms during hydrocarbon synthesis from C_1 and C_2 adsorbates. We also evaluate the kinetics and energetics for alkyne aromatization and alkene polymerization processes on supported chromium oxide catalysts. Studies are proposed to investigate the kinetics for oxygenate and non-oxygenate hydrocarbon synthesis through CO reduction on supported group VIII metals using ^{11}CO and ^{15}CO as transient probes. [4.8 FTE]

National Synchrotron Light Source Department $5,350,000

17. *National Synchrotron Light Source Operations and Development*

M. Barton

The project objective is to support operations and development of the National Synchrotron Light Source (NSLS). Operations cover: (1) operation and maintenance of the two NSLS electron storage rings and its associated injector combination of linear accelerator-booster synchrotron; (2) operation and maintenance of the photon beam lines of the vacuum ultraviolet and x-ray storage rings; and (3) the technical support of experimental users. Development of the NSLS encompasses the further improvement of the storage rings by means of new developments in high resolution photon optics, state-of-the-art monochromators, x-ray mirror systems, detectors, and so forth. The NSLS storage rings will provide extremely bright photon sources, several orders of magnitude more intense in the vacuum ultraviolet and x-ray regions than conventional sources. An extensive research and development program is necessary to optimize performance characteristics and to develop new beam line instrumentation that will permit users to take advantage of the unique research capabilities to be offered by this important new facility. This research and development effort also provides information that will support the construction of the beam lines and devices to be funded under the Phase II construction project. [53.8 FTE]

Lawrence Berkeley Laboratory
Berkeley, California 94720

Chemical Biodynamics Division $1,030,000

18. *Artificial Photosynthesis*

M. Calvin, J.W. Otvos

The project aims to devise a synthetic system for storing the energy of visible light to accomplish a photoinduced electron transfer across a phase boundary, mimicking natural chloroplasts in the process of photosynthesis. Our approaches involve the use of various kinds of phase boundary in stabilizing the primary products of photosensitized electron transfer reactions and thus preventing their back reaction. Ultimately, the energy stored in these products will be channeled by appropriate catalysts into the decomposition of water into hydrogen and oxygen, or the reduction of CO_2 to functionalized organic products. Phase boundary studies include: (1) lipid bilayer walls of phospholipid vesicles (used to keep the initial photoproducts separate), (2) surfaces of colloidal silica and various polyelectrolytes, and (3) surfaces of functionalized colloids. The surface potential of polyelectrolytes and polymeric colloids can be used to retard back-reactions of the primary products of electron transfer. They may also have advantages over colloidal silica by virtue of their adjustable charge density and useful pH range. Finally, we are studying the catalysts that will be necessary on both sides of the electron transfer assembly. We focus on porphyrin complexes of manganese, which can exist in several oxidation states and may therefore be useful in catalyzing the conversion of the primary oxidized photoproduct to oxygen. [6.0 FTE]

19. *Picosecond Photochemistry*

J.H. Clark

Proton-transfer and electron-transfer reactions of electronically excited molecules form the basis for virtually all existing and proposed methods for the photochemical fixation of solar energy. We use the techniques of picosecond laser spectroscopy to directly monitor (in real time) the dynamics of these ultrafast processes. Such studies provide insight into the details of the mechanism and kinetics of these reactions at the molecular level. This work has shown that the naphthols, substituted naphthols, and substituted phenols provide prototypical systems in which the dynamics of excited-state proton-transfer are exquisitely sensitive to subtle chemical changes. The effects of solvent environment, intermolecular and intramolecular hydrogen bonding, molecular conformation, and reactant geometry are being studied to quantify their role in excited-state proton-transfer processes. Picosecond time-resolved resonance Raman spectroscopy and time-resolved emission spectroscopy are conducted on a number of electronically excited organometallic complexes to establish the changes in geometrical and electronic structures that occur upon photoexcitation. Picosecond dynamic photoselection spectroscopy has been developed and is being used to probe the symmetries of the excited electronic states of large molecules in solution. Picosecond time-resolved emission plays an important role in the reaction mechanism as a process by which energetic species are produced or removed. This project studies the transfer of translational, vibrational, or electronic energy. Atoms or molecules are produced in excited states by a pulse of ultraviolet, visible, or infrared radiation. The time-dependent disappearance of these excited species is monitored by the detection of radiation, either from the parent species or from molecules that have been excited by collisional energy transfer. This project also supports both in-house research and assistance to outside users at the Dynamic Spectroscopy Beamline on the vacuum ultraviolet ring of the National Synchrotron Light Source. [5.8 FTE]

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26. Photochemical and Photoelectrochemical Processes for Light-Energy Conversion

T.W. Ebbesen, P.V. Kamat

Photocatalytic transformations in solution, homogeneous and heterogeneous, are investigated in order to develop and improve the performance of photoelectrochemical systems useful in conversion and storage of solar energy. Pulse radiolysis measurements, laser photolysis, and computer simulation methods are used to elucidate the dynamics of H_2 and O_2 evolution in photochemical conversion systems. Several contributing kinetic components of coupled reactions in solution are isolated for study of single reaction components and then extrapolated to the dynamics of coupled systems. Examples involve H_2 and platinum catalyst interactions and redox chemistry of viologens, which were found to influence the H_2 production under irradiation. Photoelectrochemical studies will aid the development of modified electrode surfaces with photosensitive materials and characterization of their photophysical, photochemical, and electroanalytical properties. Electrodes modified with a thin film of poly(p-phenylene sulfide) or a dye-incorporated clay film have exhibited excellent photoelectrochemical behavior. Time-resolved photoelectrochemical experiments are performed with the aid of nanosecond laser spectroscopy, spectroelectrochemistry, and cyclic voltammetry. Such studies are essential in elucidating mechanistic features and kinetic details of interfacial processes. [4.8 FTE]

27. Inorganic Photochemical Processes

G. Ferraudi

The project will elucidate the photochemical properties of coordination complexes. Studies include (1) the sequential two-photon photochemistry of coordination complexes, (2) the effect of intense magnetic fields on photochemical reactions, and (3) the photophysical and photochemical transformations of complexes with macrocyclic ligands. The sequential biphotonic excitation technique is being used to probe the time and energy relationships between long-lived excited states or long-lived reaction intermediates. Correlations between the results of time-resolved experiments and quantum yields provide unique insight into photochemical reactions that cannot be induced with monophotonic excitation. Magnetic field-induced perturbations of orbitally degenerate excited states are being used to investigate electron and energy transfer reactions (i.e., those processes involving excimers or exciplexes). Photophysical and photochemical studies are being conducted on silicon complexes with macrocyclic ligands (phthalocyanines and more simple macrocycles) as well as with coordination complexes bound to polymers. Such compounds exhibit either direct or sensitized photochemical redox reactivity for excitation in the visible region of the spectrum and are candidates for use in solar energy conversion. [7.5 FTE]

28. Microwave Studies of Radiation-Produced Radicals

R.W. Fessenden

The project uses electron spin resonance (ESR) spectroscopy to study radical structures, reaction mechanisms, reaction kinetics, and electron spin interactions. Radicals are produced by *in situ* radiolysis. Their ESR spectra provide definitive information on geometric and electronic structure. Time-resolved ESR experiments with pulsed radiation provide information on rates of radical reactions and the strengths of electron spin interactions that lead to bonding. Recent measurements on cyclohexadienyl radicals and related systems containing ^{13}C show that some aspects of the electronic structure are not yet understood; this problem will be attacked on experimental and theoretical levels. Microwave dielectric absorption methods are used to determine the degree of charge separation in photochemical intermediates to explain changes in reaction mechanism with solvent polarity. A number of excited complexes (exciplexes) are found to have smaller dipole moments than previously believed. Implications of this finding are being investigated. Microwave absorption methods are also used to measure the yield, properties, and kinetics of charge carriers photoinjected into semiconductor particles. This method provides information not otherwise available on systems of importance to solar energy conversion. [8.1 FTE]

29. Spectroscopy of Reaction Intermediates

J.L. Hardwick

This project uses modern techniques of molecular electronic spectroscopy to determine basic chemical and physical properties that affect the chemical reactivity of important molecules in combustion, photochemistry, and radiation chemistry in the gas phase. The observed spectra yield information essential for accurate monitoring and identification of some of the highly reactive species found in flames and electric discharges as well as aiding in the predictions of their reactivity based on energetic and symmetry considerations. It has been demonstrated for the first time that an examination of molecular selection rules using high resolution electronic spectroscopy provides a definitive test for ergodic behavior in small molecules. Such behavior is a crucial hypothesis of some of the most commonly used models of chemical reactivity (those based on RRKM theory) but has heretofore only been inferred from the degree of success of those theories. This result marks the first direct observation of the wholesale deterioration of quantum mechanical selection rules due to the onset of quantum chaos. [2.0 FTE]

30. Spectroscopy of Core-Excited Molecules

R.G. Hayes

Photons in the 200 to 500 eV region from the ultraviolet storage ring at the National Synchrotron Light Source (NSLS) are being used to selectively excite the ls electrons in molecules containing several first-row atoms, such as formamide ($HCONH_2$). We observe the photochemical processes that follow the excitation (especially the ionic products of fragmentation). The objective of the work is to determine the dependence of the photochemical processes on the site of core-electron excitation of the molecule and on the nature of the excitation (direct ionization vs. excitation to a resonant state). In the past year, apparatus for the experiment has been designed and constructed. Ancillary studies on the calculation of valence Auger spectra by using the MS-Xα technique to obtain the two-hole part of the Auger final-state energy have been completed. We are able to calculate well the valence Auger spectra of several first-row diatomic molecules (N_2, CO, NO, O_2, F_2, HF) and to understand the effects of hole-hole correlation in CF_4, ClO_4^{-1}, and ClO_3^{-1}. We have also studied the resonant photoemission of the valence region of MnF_2 at NSLS and have been able to interpret it as showing the dependence of photoemission resonance on covalency. [0.9 FTE]

31. *Statistical Theories of Reacting Systems*

J.J. Kozak

We will conduct a theoretical study of reaction-diffusion processes in compartmentalized systems to determine and quantify the factors affecting the efficiency of chemical-dynamic processes related to energy storage and transfer in such systems. Our approach, which is based on the theory of finite Markov processes, allows the efficiency of reaction between a diffusing coreactant and a target molecule to be studied as a function of the size of the reaction space, its dimensionality, and symmetry. We consider situations where there exists a potential of the form $v(r) = r^{\pm s}$, centered at the active site, and explore the interplay between this longer-range biasing potential and other short-range (nonspecific) chemical or cage effects in modulating the efficiency of the process. One may assess how different configurations of reaction centers on surfaces (and their relative disposition), as well as imperfections in such surfaces (terraces, kinks, ledges), can alter the turnover number for bimolecular processes. Systems having internal structure (organized molecular assemblies such as monolayers, micelles, and vesicles) are also considered. These studies will clarify experiments in which organizates may be applied in photochemical processes to affect the storage of solar energy. [6.4 FTE]

32. *Track Effects in Radiation Chemistry*

A. Mozumder, J.A. LaVerne, R.H. Schuler

The project focus is on energy deposition by low-energy electrons and its statistical variation. Such studies determine (1) the size of microscopic regions of chemical reactions for high energy electrons and (2) the geometry of heavy particle tracks. Recently we developed a technique that (for the first time) provides the range distribution calculation using the oscillator strengths of molecules. These studies establish that: (1) the relative variation is mainly determined by electron energy; (2) the distribution is very wide; and (3) typical mean ranges of a 1000 eV electron are 6.1, 7.1, and 8.4 $\mu g/cm^2$ for H_2O, H_2, and O_2. Such information is not available elsewhere in the literature. We have also determined the time dependence of electron energy during thermalization. Parallel experimental studies with heavy ions find that: (1) the HO_2 yield in water radiolysis decreases rapidly with particle energy, and (2) in benzene radiolysis the differential H_2 yield decreases with particle energy while the total yield approaches the fast electron value even though the energy transfer remains high. These findings necessitate reconsideration of track structure in terms of core energy density rather than the traditional energy partition between the core and delta electrons. [3.1 FTE]

33. *Influence of Ordered Molecular Assemblies on Chemical Processes*

L.K. Patterson

The behavior of photo- and radiation-induced transients is investigated in a variety of hetrogeneous systems: monolayers, micelles, and liquid crystals, each of which exhibits different facets of molecular organization. The objective is to elucidate the ways in which molecular assemblies (for which the systems mentioned are elementary models) may be used to excercise control over reaction rates and mechanisms. At present, spread monolayers receive the greatest attention as they provide the means for controlling the degree of organization within the system and for monitoring associated thermodynamic parameters. Factors governing J-aggregate formation in cyanine dyes (e.g., coaggregate, surface pressure, temperature) have been evaluated by means of fluorescence spectroscopy. These studies are being extended to reflectance measurements. Energy transfer in monomeric and J-aggregate systems has been characterized. A continuing time-resolved study with pyrene-labeled probes in lipid monolayers has provided information on the orientation of the pyrene in the layer, and a simple technique for monitoring diffusion of the probe under various conditions. [9.5 FTE]

34. *Radiation Chemistry Data Center*

A.B. Ross, W.P. Helman, G. Hug, I. Carmichael

The Radiation Chemistry Data Center compiles and evaluates data from the scientific literature on radiation chemistry and quantitative photochemistry and publishes bibliographies, data compilations, and critical reviews. Emphasis is on kinetic and spectroscopic data for transients in solution, the effects of ionizing radiation on chemical systems, and photochemical and photophysical processes in solution. The Center builds up bibliographic and numeric data bases; the Bibliographic Data Base (RCDCbib) provides retrospective searches, available from the Center or through the on-line network DOE/RECON. The Biweekly List of Papers on Radiation Chemistry and Photochemistry, the printed version of RCDCbib, provides current-awareness service to subscribers. Triplet-triplet absorption spectral data for organic molecules have been compiled and evaluated. Rate constants for transient radicals in aqueous solution are compiled and evaluated in collaboration with scientists from other laboratories. Outside collaborators are also involved in compilation and evaluation of rate constants for quenching of excited states of metal complexes in solution, and one-electron reduction potentials for radicals in aqueous solution. Numeric data bases are associated with a registry file for chemical species represented in the data files. Automated selection, tabulation, and correlation of the data files with the bibliographic and chemical registry files aids the compilation, evaluation, and publication process. [4.0 FTE]

35. *Radiation Induced Chemical Reactions*

R.H. Schuler, G.N.R. Tripathi, L.K. Patterson

A wide variety of chemical reactions induced by the absorption of ionizing radiation are being examined using the Laboratory's broad base of highly developed chemical and instrumental methods (absorption spectrophotometric, conductivity, ESR, laser Raman, and chromatographic methods) for examining intermediates in time-resolved studies and for analysis of ultimate products. Currently, considerable emphasis is being given to time-resolved resonance Raman experiments that permit both structural and kinetic studies on short-lived free radicals. Recent Raman studies have made it possible to determine the dissociation energy of $Cl_2\cdot^-$, $Br_2\cdot^-$, and $I_2\cdot^-$ radical in aqueous solution. The vibration structures of prototype chemical systems such as phenoxyl and anilino radicals and the semiquinone radical anions are also being examined. Improvements in dosimetry and time resolution at the LINAC facility allow complementary absorption spectroscopic and conductometric pulse radiolytic studies to be carried out at nanosecond times. Studies are also being carried out at very high pulse intensities to examine the products of second-order reactions between phenoxyl radicals using a Febetron as a radiation source. [18.5 FTE]

Solar Energy Research Institute
Golden, Colorado 80401

Solar Fuels and Chemicals Research Division — $675,000

36. Photophysics and Photochemistry of Porphyrins and Model Systems for Artificial Photosynthesis
J.S. Connolly

This project is concerned with fundamental studies of energy- and electron-transfer processes of excited states in a variety of porphyrin-related systems. The focus is on detailed photophysical properties of porphyrins and on light-induced electron transfer in synthetic models of photoreaction centers. The goal is to contribute to an improved understanding of the molecular properties required for efficient light-induced electron transfer in artificial photosynthesis. Laser flash photolysis, fluorescence, and spectroscopic studies are being carried out on covalently linked porphyrin-quinones and on their unlinked constituents to sort out the effects of photophysical properties, redox potentials, molecular geometry (distance and orientation), temperature, and solvent properties on the kinetics and mechanisms of light-induced electron transfer and subsequent charge stabilization. [0.9 FTE]

37. Modified Semiconductor Electrodes for Solar Energy Utilization
A.J. Frank

This research program addresses the fundamental problems of the photoinstability of n-type semiconductors, the high overpotential associated with the water splitting reaction, the low quantum yields from recombination of electron-hole pairs at the electrode-electrolyte interface, and the energetics and dynamics of charge transfer through conductive polymer films on electrode surfaces. Interfacial chemistry, energetics, and surface dynamics are established by photoelectrochemical measurements, end-product analyses, and surface characterization studies. Information obtained from the physicochemical investigations provides guidance for chemically modifying the semiconductor surface to improve photostability and kinetics of desirable redox reactions. The utility of coating the semiconductor surface with electrically conductive polymers in combination with catalytic dispersions of several transition metals is demonstrated for the visible light-induced water-cleavage reaction. Further development and study of conductive polymers and catalytic surface structures involving coordination metal complexes are in progress. The degree of stability and catalytic activity produced is remarkable and provides encouragement for the potential application of catalytic conductive polymer films to practical photoelectrochemical devices for solar energy conversion. [1.0 FTE]

38. Basic Photoelectrochemistry Research
A.J. Nozik, J.A. Turner

Basic research in photoelectrochemistry is being conducted in: (1) hot carrier effects, (2) superlattices and multiple quantum well photoelectrodes, and (3) colloidal and particulate semiconductors. Hot electron injection into aqueous electrolyte has been demostrated for p-InP electrodes; the kinetics for H_2 evolution are improved, but they are not as good as that produced by catalytic metals on the surface. Hot hole injection from photoexcited dyes adsorbed on n-GaP surfaces was demonstrated; a model for this process was developed and fitted to the data. Large quantization effects were found for the first time in photoelectrochemical systems using $GaAs/GaAs_{1-x}P_x$ superlattice electrodes. The photocurrent spectra showed discrete peaks that fitted very well to the theoretical energy-level structure of the GaAs quantum wells. Photoelectron transfer from the discrete levels into the electrolyte is a hot carrier process that could produce high conversion efficiencies as theoretically predicted. Quantization effects in small CdS semiconductor colloids were found for particles < 50 Å. These colloids were studied for the first time by stopped-flow spectrometry, which permitted determination of the kinetics of particle growth and evolution of size quantization effects. [3.6 FTE]

Chemical Physics

Ames Laboratory
Ames, Iowa 50011

Fundamental Interactions Program — $660,000

39. Statistical Mechanics of Non-Equilibrium Systems
D.K. Hoffman

Statistical mechanics is used to develop a kinetic theory of polyatomic gases in which transport, relaxation, and reactive processes are of interest. Classical and quantum mechanical scattering theory is used in the development of collision models to describe energy transfer and reaction between molecules with internal structure. The dynamics and statistics of distributions of molecules adsorbed on surfaces under nonequilibrium conditions is analyzed via master equations. Such a theory is important for the appropriate interpretation of surface spectroscopic data associated with these processes. This project includes an investigation of the effect of surface coverage on the nature of binding sites, an exploration of interactions between adsorbed surface species, a study of surface migration and cluster formation, and adsorbate effects on the catalytic properties of surfaces. These models for irreversible lattice processes are also applied to other (non-surface) systems. [1.95 FTE]

40. Atomic, Molecular, and Free Radicals: Crossed Beam Kinetics
C.Y. Ng

This project involves the study of the mechanisms and dynamics of fundamental processes that are relevant to combustion and plasma chemistry. Different experimental approaches combining the merits of the molecular beam method, photoionization and time-of-flight mass spectrometry, and laser spectroscopy are being developed in order to measure reaction cross sections of elementary chemical reactions at well-defined collision energies and internal states of the reactants and to identify the kinetic and internal energy distributions of the products. Research includes (1) high-resolution photoionization studies of hydrocarbon clusters and high-temperature vapors, (2) state-selected and state-to-state ion-molecule reactions (emphasizing charge exchange and proton transfer reactions), (3) vibrational relaxation of simple molecular ions, (4) laser photofragmentation spectroscopy of polyatomic molecules, and (5) neutral-neutral interactions by the crossed molecular beam method. [3.43 FTE]

41. *Molecular Bonding Theory*
K. Ruedenberg

Properties of molecules such as geometric shapes, the behavior in electrical and magnetic fields, optical spectra, and in particular the energy changes that occur during chemical reactions are determined through quantum mechanical *ab initio* calculations of their electronic structures. Energy hypersurfaces that determine the course, directions, and rates of chemical reactions are mapped out as functions of atomic displacements, and their general features are elucidated. Reaction energies, activation energies, transition states, and elusive intermediates are predicted. The electronic rearrangements that occur along reaction paths and their energetic and kinetic implications are analyzed. Fundamental and computational advances are made in many-electron quantum mechanics (including electron correlation) to establish practical methods for predicting reaction mechanisms with an accuracy that is useful to experimental chemists. Quantitative implementations are developed for interpretative chemical concepts by determining rigorous contributions to interatomic interactions to provide a reliable basis for the intuitive anticipation of *ab initio* predictions. These methods are used to study oxidation-reduction reactions, exchange reactions, and isomerizations involving carbon, nitrogen, oxygen, hydrogen, and fluorine atoms. Of particular interest are reactions occurring in combustion, in the atmosphere, and during hydrogenations. [2.76 FTE]

42. *Ion Chemistry: Mass Spectroscopy*
H.J. Svec, G.D. Flesch

This research involves the ion chemistry of inorganic, organometallic, and organic compounds, and ions and complementary neutral fragments produced by electron bombardment. The latter leads directly into the chemistry of highly excited molecules and free radicals. The results bear directly on the origin of aromatic heterocyclic hydrocarbons produced in the combustion of natural gas, oil, wood, and coal under fuel-rich conditions. [1.45 FTE]

Argonne National Laboratory
Argonne, Illinois 60439

Chemistry Division **$1,896,000**

43. *Theoretical and Computational Chemistry*
T.H. Dunning, Jr., R.A. Bair, M.J. Davis, L.B. Harding, R.L. Shepard

This project concentrates on theoretical studies of the energetics and kinetics of chemical reactions emphasizing reactions of importance in the oxidation of hydrogen and simple hydrocarbon fuels. The main focus of the project is on calculation of accurate molecular interaction potentials, study of the chemical dynamics on the computed (or other realistic) potential energy surfaces, and characterization of the molecular species (including ephemeral species) involved. Goals include the development of a qualitative understanding of the fundamental laws governing chemical change and the development of quantitative techniques for calculating the energetics and dynamics of these elementary chemical processes. There is also a continuing effort devoted to developing the computational methodology needed to accurately predict the kinetics of chemical reactions. [7.5 FTE]

44. *High-Resolution Spectroscopy and Intramolecular Dynamics*
J.P. Hessler, F.S. Tomkins

The project objectives are to use high-resolution laser techniques that generate vacuum ultraviolet light (1) to elucidate the complex dynamical processes needed to describe the behavior of excited polyatomic molecules and (2) to study unimolecular chemical reactions that proceed via two decay channels. At present, one of these channels must involve the production of atomic hydrogen. To monitor dynamical processes, we excite specific predissociative and/or Rydberg states of polyatomic systems cooled by supersonic expansion techniques and monitor the evolution of the polyatomic system. Unimolecular chemical reactions that evolve hydrogen will be studied in an ultra-high-purity shock tube. Rates of reactions and the absolute branching ratios of competing reactive channels will be measured using our laser techniques to perform time-resolved absorption measurements of the concentration of atomic hydrogen. [1.9 FTE]

45. *Molecular Beam and Metal Cluster Chemistry Research*
S.J. Riley, E.K. Parks, K. Liu

The study of heterogeneous catalysis on a molecular level is pursued. Beams of catalytically active naked metal (nickel, chromium, vanadium, silver, copper, aluminum, iron) atom clusters containing 2 to 200 atoms are generated by pulsed lasers, and their physical and chemical properties are characterized by laser based, in-flight diagnostic techniques. Spectral and electronic properties are determined and experimental results are correlated with theoretical calculations. Mechanisms, energetics, and kinetics of cluster chemical reactions and of adsorption and catalytic processes on cluster surfaces are determined by the flow tube technique. The transient products are identified by laser ionization mass spectrometry. [5.6 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Applied Science Department $610,000

46. *Kinetics and Mechanisms of Alternative Fuels Combustion*
R.B. Klemm, J.V. Michael, J.W. Sutherland

The aims of this project are (1) to measure absolute rate constants for elementary combustion-related reactions over a wide temperature range and (2) to investigate mechanistic factors involved in gas phase combustion and pollutant formation processes. Emphasis is on alternative fuels that comprise a range of fuel types, including alcohols and hydrocarbon synfuels. In pursuing the goals of this project, a facility has been developed that features a variety of experimental techniques including: (1) flash photolysis-resonance fluorescence (FP-RF); (2) discharge flow-resonance fluorescence (DF-RF); (3) flash photolysis-shock tube (FP-ST); and (4) discharge flow-photoionization mass spectrometry (DF-PIMS). The FP-RF and DF-RF methods are used in determining specific rates of elementary atom-molecule and radical-molecule reactions over a wide temperature span, ~200 to 1100 K. The recently developed FP-ST apparatus extends the high temperature capabilities for direct rate measurements by a significant extent. With this device, kinetic studies are performed over a temperature range from ~800 to 2000 K; and thus these measurements overlap the temperature range of the other, more conventional techniques used in this project. The DF-PIMS method is used in an effort to make direct observations of reactants and products for elementary reactions to investigate the relevant reaction mechanisms. This DF-PIMS experiment uses the National Synchrotron Light Source. [6.0 FTE]

Chemistry Department $2,750,000

47. *Theoretical Chemistry*
S. Ehrenson, J.T. Muckerman, M.D. Newton

The project objectives are to apply theoretical methods (1) to the study of energy flow in chemical reactions and (2) to the elucidation of molecular interactions involved in the storage and interconversion of energy in the gas phase and in condensed phases (including phenomena associated with charged species). Methods include (1) *ab initio* and semiempirical calculations of the energies and structures of molecules in specific electronic states and (2) classical and semiclassical treatments of the nuclear motion in kinetic processes involving these systems. Many of the techniques currently being developed and applied in this project play an important role in analyzing and interpreting experimental data obtained at the National Synchrotron Light Source (NSLS), the High Flux Beam Reactor (HFBR), and in other experimental programs in the Department. [6.0 FTE]

48. *Ion-Molecule Reactions with Applications to Fusion Energy Systems*
L. Friedman, R.J. Beuhler

A high molecular weight mass spectrometric facility has been developed that is capable of mass analysis and sensitive detection of singly charged ions with masses up to ~200,000. Ion source techniques have been developed for the generation of a wide variety of cluster ions with mass distributions by free jet expansion of weakly ionized plasmas. These techniques are being used to investigate energy transfer in the impacts of cluster ions on solid surfaces. Electron microscopy is being used to study morphology of craters and holes generated in thin target films by evaporation or sputtering processes that provide a channel of target cooling competitive with thermal conduction. The major goal of this project is to investigate the properties of the transient hot atom assemblies generated by cluster ion impacts. Practical applications of these impacts are also of interest and include their use to produce very small holes, to remove very thin layers of surface, and to alter the chemical architecture of the bombarded surface. In addition, cluster impacts provide a means of investigating a variety of high temperature desorption phenomena. [6.7 FTE]

49. *Gas-Phase Photoionization and Photoelectron Spectroscopy of Molecules and Clusters*
J.R. Grover, M. White

The first objective of this project is to understand how molecules initially approach each other on the way to a reactive collision. Such understanding is necessary if accurate predictions of reaction rates are to be made. Measurements of the enthalpy of binding of van der Waals complexes and clusters of the reactive molecules are being made using the tunable, monochromatic radiation from the gas phase beamline on the vacuum ultraviolet storage ring at the National Synchrotron Light Source. A subsidiary goal is to obtain previously unknown heats of formation for free radicals and molecular fragments that appear as reaction products or energetic reaction intermediates. The second objective is to explore and characterize the photoexcitation and subsequent ionization processes of resonantly excited molecules. A general photoelectron spectroscopy study of the ionization dynamics of neutral molecular ground and excited states using both synchrotron and laser radiation is underway. From the observed electronic and vibrational state distributions of the product ions, it is possible to investigate in detail the dynamics of the interaction between the anisotropic field of the molecular ion core and photoelectron. [4.4 FTE]

50. *Structure and Bonding of Solids and Molecules on Their Surfaces*
J. Hrbek, T.K. Sham

The main project objective is to improve the understanding of (1) the electronic interactions between surfaces and adsorbates and (2) the interactions among atoms in condensed matter, emphasizing technologiclly important materials. Identification of molecular structure of surface intermediates, active sites on surfaces, and the effect of promoters and poisons on surface selectivity and activity will make it possible to understand and control the chemistry of surfaces. These studies are being carried out through photoelectron spectroscopy, thermal desorption, electron diffraction, vibrational spectroscopy, and the development and application of synchrotron radiation spectroscopies (e.g., photoelectron and x-ray absorption, XANES, and EXAFS). Results of these studies are directly related to kinetic and mechanistic aspects of chemical reactivity and catalysis. [3.4 FTE]

51. *Chemical Crystallography*
T.F. Koetzle, A. Kvick, R.K. McMullan

Neutron and x-ray diffraction methods are used to solve significant problems in crystal and molecular structure. Emphasis is placed on structures where hydrogen and other light atoms are important and on disordered or partially-ordered structures, since in these areas neutron diffraction, alone or in combination with x-ray diffraction, has unique advantages for determining molecular structure and investigating chemical bonding. In addition, access to the chemical crystallography beamline at the National Synchrotron Light Source will open up new areas for x-ray diffraction studies. Examples of systems investigated under the crystallography project include organometallic compounds, transition-metal hydrides, zeolites, fast-ion conductors, and dielectric materials. [4.8 FTE]

52. *Spectroscopy and Structure of Short-Lived Chemical Intermediates*
T. Sears

Studies of the structure and reactivity of molecular fragments are important to the understanding of gas phase chemical reaction pathways and rates. Infrared laser techniques are applied to the study of these species, which are usually unstable and are present only in trace quantities in reaction mixtures. Analysis of the spectra will lead to details of molecular structure, intra- and inter-molecular potential functions, and estimates of the concentrations of reaction intermediates involved in the course of reactions important in combustion and in semiconductor technology. [1.5 FTE]

Lawrence Berkeley Laboratory
Berkeley, California 94720

Applied Science Division **$135,000**

53. *Unimolecular Kinetics and Ignition Chemistry*
N.J. Brown

Combustion chemistry consists of complex chain mechanisms involving radical species. The inherent difficulties encountered in high temperature environments and the large number of species involved in hydrocarbon oxidation make the study of combustion chemistry difficult. One activity of the current research focuses on applying theoretical chemical kinetics to study high temperature kinetics important in combustion. Emphasis is on investigating the dynamics of reactions using classical trajectories. Unimolecular and bimolecular reactions are investigated with realistic potential energy surfaces. Special emphasis is on elucidating the role of molecular angular momentum of intramolecular and intermolecular energy transfer processes. Rate coefficients for reactions important in combustion are also determined with statistical theories. Further activity concerns investigating the ignition chemistry of hydrocarbon-air mixtures. Identification of the principal elementary reaction steps that occur during ignition of hydrocarbon-air mixtures and determination of the corresponding rate coefficients are required to achieve an understanding of this phenomenon. Ignition will be investigated in a constant volume and steady-state system. Time-resolved evolution and decay of radical species will be monitored with a molecular beam mass spectrometer and by other spectroscopic methods. [1.0 FTE]

Materials and Molecular Research Division **$2,394,000**

54. *Energy Transfer and Structural Studies of Molecules on Surfaces*
C.B. Harris

The goal of this research is (1) to study the mechanisms responsible for transfer of energy from the excited states of molecules to metal surfaces and (2) to develop new laser techniques for probing molecule-surface interactions. The research is both theoretical and experimental, and includes non-linear optical and picosecond laser techniques in addition to a variety of standard surface science tools for characterizing molecule-surface interactions. Recent work has centered on the development of picosecond infrared lasers, the elucidation of the mechanism of surfaced enhanced photochemistry, and the breakdown of classical dielectric response theory for explaining energy transfer from molecules to noble metal surfaces. The latter studies have resulted in a classification scheme in which molecular excited states that produce intraband electronic excitations transfer energy to electrons localized near the metal surface, while those excited states that can access direct interband excitations transfer energy to electrons throughout the bulk of the metal. Results have a direct bearing on high speed technological devices and materials and on other problems of general interest (e.g., the dynamics of surface photoemission and the optical properties of thin films). [2.2 FTE]

55. *Crossed Molecular Beams*
Y.T. Lee

The major focus of this research project is to elucidate detailed dynamics of simple elementary reactions that are theoretically important and (using the molecular beams method) to unravel the mechanism of complex chemical reactions or photochemical processes that play an important role in many macroscopic processes. Molecular beams of reactants are used to study individual encounters between molecules or to monitor photodissociation events in a collision-free environment. Most of the information is derived from measurement of the product fragment energy and angular distributions using a unique molecular beam apparatus designed for these purposes. Recent activities are centered on the following areas: (1) the direct probing of transition states of the F + H_2 reaction through the experimental observation of quantum mechanical resonance phenomena; (2) the mechanisms of elementary chemical reactions involving oxygen atoms with unsaturated hydrocarbons; (3) the dynamics of chemical reactions of electrochemically excited atoms; (4) the primary photochemical processes of polyatomic molecules, radicals, and ions; (5) intramolecular energy transfer of chemically activated and locally excited molecules using overtone excitation processes; and (6) the interaction potential of open shell atoms with rare gas atoms. [10.0 FTE]

56. *Molecular Interactions*
W.A. Lester, Jr.

The project objective is to extend fundamental knowledge of the interactions and dynamics that govern energy transfer, reactive, and photodissociative molecular processes. The approach combines the use of potential energy surfaces constructed using rigorous non-empirical methods (*ab initio* Hartree-Fock, multi-configuration Hartree-Fock, and configuration interaction) with quantum, semi-, and quasi-classical approaches to nuclear dynamics. Current efforts focus on (1) single-photon photodissociation of C_2N_2 using *ab initio* MCHF potential energy surfaces and a recently developed adiabatic treatment of photodissociation dynamics; (2) extension of the adiabatic photodissociation development to bimolecular chemical reactions; (3) determination of cross sections for rotational and vibrational energy transfer by atom impact for electronically excited molecules (He-H_2, HD($B^1\Sigma_u{}^+$)); and (4) the application of Monte Carlo methods to the computation of potential energy surfaces, properties of individual molecules, and collision cross sections. [3.9 FTE]

57. *Theory of Atomic and Molecular Collision Processes*

W.H. Miller

This research is primarily involved with the development of theoretical methods and models for describing atomic and molecular collision processes. Specific topics of interest include the theory of inelastic and reactive scattering, collision processes involving electronically excited atoms or molecules, collisional ionization phenomena, statistical theories of chemical reactions, scattering of atoms and molecules from surfaces, and the interactions of molecular systems with high power laser radiation. Much of this research is involved with the development and application of a general semiclassical mechanics that allows one to combine classical mechanics and quantum mechanics in a correct and useful manner. This has been extremely successful in providing an understanding of the various quantum effects that are seen in molecular phenomena, and it also often provides simpler computational methods for carrying out quantitative calculations. Certain research topics are more amenable to a completely quantum mechanical approach, and these sorts of theoretical techniques are also used. The ability to understand, and thus to model and to predict, chemical kinetics phenomena in the gas phase has widespread practical importance in a number of different areas. Among these are atmospheric chemistry and physics, interactions of molecules with strong laser fields, and energy transfer and chemical reactions in flames and combustion. [2.9 FTE]

58. *Selective Photochemistry*

C.B. Moore

The fundamental goals of this project are to understand the photophysics of selective excitation of molecules, the dynamics of energy transfer and specificity loss, and the chemical reactions of excited states. The nature of the energy states of molecules as a function of excitation energy and of molecular size and structure determines the intramolecular flow of energy. The spectra of vibrationally excited molecules are studied by laser-based methods in order to determine the strength of coupling of one vibrational mode to another and to elucidate the rates and sequences of energy flow among all modes of an excited molecule. Unimolecular reaction rates are measured. An understanding of the competition between energy transfer and unimolecular reaction as a function of excitation energy, molecular size, and chemical constitution is sought. The mechanism and selectivity of bimolecular reaction processes is often revealed by the dependence of reaction rates on quantum state, isotopic substitution, and temperature. Many photochemical and combustion processes involve the formation of short-lived reaction intermediates or collision complexes. Laser flash kinetic spectroscopy is used to identify transient species and measure their reaction rates. The results are useful in the modeling of combustion processes and of photochemical reactions such as CH bond activation by organometallic photoproducts. [2.8 FTE]

59. *Physical Chemistry with Emphasis on Thermodynamic Properties*

K.S. Pitzer

The project objective is the discovery and development of methods of calculation of thermodynamic and related properties of important chemical systems by use of quantum and statistical mechanics together with experimental measurements for key systems. Primary emphasis will be on ionized systems, electrolyte solutions, and plasmas. Systems comprising fused salts mixed in any proportion with water are being studied experimentally and with semiempirical theory. Recently the critical points for pure NaCl and KCl were predicted from a combination of rigorous statistical thermodynamics (for the vapor) and an extrapolation of the empirical equations (for the liquids). With guidance from corresponding states theory, a fused salt-polar liquid system was discovered with a critical point at 140°C where detailed laboratory study is feasible. Earlier advances yielded improved equations for electrolyte solutions, which are now being applied to a wide variety of systems of industrial or geological interest (including geothermal brines). Recent efforts also included relativistic quantum mechanical methods for calculating energies, bond distances, and other properties of the ground and excited states of molecules containing very heavy atoms where the conventional nonrelativistic methods are inadequate. Such results are important in evaluating possible laser systems and for models of catalytic entities including heavy atoms (e.g., platinum). [2.2 FTE]

60. *Spectroscopy and Structures of Reactive Intermediates*

R.J. Saykally

The principal objective of this project is to study spectra, structures, and properties of elusive reaction intermediates that are of importance in combustion processes. Present emphasis is on the development of three powerful new spectroscopic techniques for detecting very low concentrations of such reactive intermediates. A far-infrared laser magnetic resonance (LMR) spectrometer employing selective ultraviolet photolytic generation of the reactive species is presently being tested; optimization of the experimental parameters for study of the hydroxyl radical has been accomplished. Extension of this approach for the study of important carbene species (HCOH, HCCN, CH_2) is in progress. A totally new laser spectroscopy experiment has been developed. Molecular beam laser electronic resonance, in which ultra cold (10 to 50 K) reactive molecules are generated in supersonic beam inside the cavity of a far-infrared laser and rotational transitions are tuned into resonance with the laser with a large dc electric field, compliments the capabilities of LMR for the study of reaction intermediates. The system is being tested on stable molecules (CH_3F, PH_3) and will be extended to prototype reactive intermediates (OH, CH, CH_2) in the near future. The first measurement of the dipole moment of methylene (CH_2) is anticipated. [3.2 FTE]

61. *Potential Energy Surfaces for Chemical Reactions*
H.F. Schaefer, III

This research project has two goals, related yet distinct. The first goal is the development of new theoretical and/or computational methods for describing what electrons do in molecules. The single outstanding problem in the field is the correlation problem, that of formulating models for going beyond the single-particle or Hartree-Fock approximation. The second goal is to apply these theoretical methods to significant problems of broad chemical interest: (1) model theoretical studies of chemisorption, metal clusters, and organometallic species; and (2) potential energy surfaces that govern gas-phase chemical reactions. Research in the former area is ultimately aimed at a truly molecular understanding of catalysis, a subject pertinent to future energy requirements, but sometimes approached by trial and error methods. In the latter area, research sometimes tends toward molecules potentially important in combustion or atmospheric chemistry and the development of high power laser systems. Theoretical chemistry has become a significant source not only of broad generalities, but also of specific predictions concerning molecular systems that may be very important, but inaccessible to experiment. [4.8 FTE]

62. *Photoelectron Spectroscopy*
D.A. Shirley

The major project objective is to conduct exploratory research on the interaction of vacuum ultraviolet and soft x-ray radiation with matter, emphasizing synchrotron radiation and photoelectron spectroscopy. The project also supports the national programs through innovation and development of new experimental methods based on synchrotron radiation in the energy range 10 to 4000 eV, and through the training of doctoral candidates in the use of synchrotron radiation. The reaction of radiation in this energy range with matter yields (as one reaction product) an unbound electron in a highly-excited final state. The further interaction of this electron with the other reaction product(s) can provide unique and definitive information about both reactants and products. Focus is on (1) understanding of electron correlation in atoms and small molecules, including the characterization of continuum resonances and correlation satellites and (2) characterization of the atomic and electronic structure of surfaces. This includes both structural studies by photoelectron diffraction (ARPEFS) and electronic structure determinations on and near the surface. Related supportive research includes photoelectron spectroscopy in molecular beams and high-resolution electron energy loss spectroscopy on surfaces. [10.5 FTE]

Lawrence Livermore National Laboratory
Livermore, California 94550

Division of Chemical Engineering **$40,000**

63. *Chemical Kinetics Modeling*
C.K. Westbrook

This project focuses on computer modeling of chemical kinetics of combustion in laboratory and practical systems. Particular emphasis is placed on hydrocarbon fuels that are widely used in present combustion devices. Construction and validation of comprehensive reaction mechanisms for these fuels will identify those elementary reactions on which the computed results are most dependent and, therefore, merit the closest attention from experimental and theoretical research. Experimental data from shock tubes, plug flow reactors, stirred reactors, laminar flames, and detonations are used to test and validate the reaction mechanisms. Fuels to be examined include n-pentane, n-octane, isooctane, ethanol, and propionaldehyde. Once the reaction mechanisms have been validated thoroughly, they are used to examine the role of chemical kinetics in practical combustion systems. Past applications have considered heat transfer and unburned hydrocarbon emissions from automobile engines, kinetic inhibition of flames and detonations, and the influence of pressure on combustion rates. Applications in progress include the kinetics of engine knock in internal combustion engines, kinetics of cool flames and multistage ignition, and the influence of pressure on combustion rates. Applications in progress include the kinetics of engine knock in internal combustion engines, kinetics of cool flames and multistage ignition, and the influence of fuel molecular structure on various combustion parameters. [0.3 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Chemistry Division **$385,000**

64. *Molecular Research with Electron Spectroscopy*
T.A. Carlson, M.O. Krause

The project studies the photoelectron dynamics of molecules and metal vapors using angle-resolved photoelectron spectroscopy and synchrotron radiation. Phenomena receiving particular attention include: (1) the Cooper minimum, (2) shape resonances, (3) autoionization, (4) correlation satellites, and (5) interchannel coupling. Systematic studies are being pursued on halogen acids, freons, nitrous oxide, and various metal vapors including silver, gallium, lead, and some 3d transition metal elements. Supportive calculations using the multiple scattering Xα method are being performed and correlated with observed cross sections and angular distribution parameters. Improved computer handling of the experiment has allowed the introduction of constant-ionic-state techniques. Besides providing fundamental information in atomic and molecular science, the project supplies data and ideas for studying molecules adsorbed on surfaces, clarification for solid state properties in metals, and an understanding of clusters. [2.5 FTE]

Sandia National Laboratories
Livermore, California 94550

Combustion Research Facility **$5,475,000**

65. *Flame Dynamics Research*
R. Cattolica, W. Flower, S. Johnston

The purpose of this research is to investigate the spatial and temporal interactions between chemical species, temperature, and fluid motion as they occur in flames. Included are the dynamics of carbonaceous particulates in sooting flames and the ignition, free propagation, and quenching of transient gas-phase flames. An important aspect includes the development and application to flames of advanced optical diagnostics such as time-resolved, planar, laser-induced fluorescence, and diffusion broadening spectroscopy. Fluorescence imaging has been used to study the chemical structure of a laminar flame interacting with a vortex ring. The time-dependent generation and evolution of the OH molecule during the interaction was observed. Comparison of these results with the modeling predictions generated using the vortex dynamics computational method has been made. Soot size and number density, and the effect of increasing pressure on these quantities, have been determined in a laminar diffusion flame. Local soot formation rates have been determined in laminar diffusion flames using laser-velocimetry flow-field measurements and light-scattering measurements of soot concentration. Species thought to be responsible for soot particle surface growth have been detected using coherent anti-Stokes Raman spectroscopy. [3.0 FTE]

66. *Turbulent Reacting Flow Research*
R. Dibble, R. Schefer, S. Johnston

This research is directed toward an increased understanding of the coupling between the chemical kinetic and turbulent transport processes occurring in chemically reacting flows. The long-term goal is to use this understanding to improve predictive capabilities for turbulent combustion. A new laboratory incorporating a vertical flame tunnel (and making use of the Combustion Research Facility dye laser) is fully operational. Multi-species Raman concentration and temperature measurements, combined with simultaneous velocity determinations, have been compared with model predictions to estimate the influence of chemical nonequilbrium on mean turbulent flame quantities. One- and two-dimensional imaging of major and minor species is producing new insight into mechanisms of local flamelet burning and extinction. A chemically reacting turbulent flow cooperative group comprised of participants from private industry, universities, and Sandia National Laboratories has been formed and meets on a regular basis. [3.0 FTE]

67. *Combustion Research Facility (CRF) Operations and Visiting Scientist Support*
G. Drummond, D. Benthusen

This project sustains Combustion Research Facility (CRF) operations and visitor support. Central to operations are: (1) provision and operation of the CRF central lasers; (2) operation and maintenance of CRF VAX computers, associated minicomputers, and a terminal network system; (3) staffing of shop and analytical laboratories; and (4) maintenance of the safety and control system. Equal emphasis is given to a visitor support program dedicated to transfer of technology (developed at the CRF) to interested industry and universities. Transfer takes place (1) through short courses in specialized areas, workshops on relevant topics, and combustion-related symposia and technical meetings and (2) by providing support to visiting scientists (including technical, scientific, and engineering staff dedicated to the visitor project, administrative assistance, computer time, and shop work). [13.0 FTE]

68. *Combustion Research Facility (CRF) Diagnostics Research: Coherent Raman Processes*
R.L. Farrow, R.P. Lucht, R.E. Palmer

This project aims at developing coherent Raman diagnostic techniques in support of CRF programs. Detailed studies are made of the significance of several factors for experiments using CARS, a leading technique for time-resolved measurements of temperature and major species concentrations. These factors include laser photon statistics, Stark effects, laser lineshape convolutions, *in situ* normalization, and interferences between resonant Raman and nonresonant background contributions. The first CARS measurements of flame-generated acetylene, an important soot precursor, have been made, resulting in the determination of spectral constants for hot bands unavailable from room temperature data. The modification of CARS spectra at high pressure due to collisional narrowing is being quantified in detail using high-resolution CARS and high-resolution inverse Raman spectroscopy, so that measurements in high-pressure environments (e.g., internal combustion engines) can provide more accurate results. Inverse Raman spectroscopy is also being used to develop a high-resolution data base of spectral parameters for important combustion species such as nitrogen, carbon monoxide, hydrogen, and water vapor. [3.0 FTE]

69. *Flame Chemistry: Modeling and Experiments*
G.A. Fisk, J.A. Miller, R.J. Kee, L.R. Thorne, D.W. Chandler

The principal objective of this research is development of comprehensive models for the chemical processes that govern flames. Emphasis is on production and destruction of pollutants in flames. New numerical techniques have been implemented to provide fast and accurate methods for solving the one- and two-dimensional laminar flame equations (including sensitivity analyses), thereby facilitating comparisons with a wide range of experimental results. Laboratory studies emphasize the use of advanced laser probes for measurements of radical and stable species concentration profiles in flames. Other techniques, including molecular beam-mass spectrometry and Fourier transform infrared spectroscopy, are also employed. During the past year, a new CW laser source was developed as a near-ultraviolet diagnostic and used to obtain laser-induced fluorescence (LIF) spectra of CH and CN in a series of low pressure flame experiments. The effect of a molecular-beam-mass-spectrometer sampling probe on the structure of a flat H_2, O_2, Ar, HCN flame was determined quantitatively using LIF to map CN rotational distributions near the probe. Analysis and modeling of the structure and extinction limit of counterflow diffusion flames identified the mechanism of stretch-induced extinction and the role of oxygen breakthrough. [4.0 FTE]

70. *Chemical Kinetics and Dynamics*
G.A. Fisk, F.P. Tully, R.A. Perry, D.W. Chandler, C. Melius, J.A. Miller

This research is directed at understanding fundamental chemical processes of importance in combustion. Laser photolysis is used to produce radicals in slow-flow reactors, and the kinetics and mechanisms of ensuing radical-molecule reactions are followed by chemiluminescence and laser induced fluorescence. Laser photoexcitation is used to produce energetic and reactive molecules whose subsequent chemistry (relaxation and reaction) is followed in time via state specific detection of products. Theoretical methods are also used to analyze pathways of combustion reactions. BAC-MP4 (bond additivity corrected-fourth order Moller-Plesset perturbation theory) calculations are used to determine the properties of stationary points (stable molecules and saddle points or transition states) on the potential energy surfaces of critical reactions. Statistical methods are used to predict rate coefficients and branching ratios from this potential surface information. In addition, the influence of inter- and intra-molecular energy transfer on unimolecular reactions is studied using dynamical methods. [4.0 FTE]

71. *Combustion Research Facility (CRF) Diagnostics Research: Advanced Methods*
J.E. Goldsmith, M.L. Koszykowski, A. Lau, F.P. Tully, R.E. Palmer

This project supports three broad areas of diagnostic research: (1) development of new multiphoton nonlinear techniques for detecting trace species in combustion environments; (2) advanced methods for kinetics studies; and (3) theoretical studies in support of CRF projects. In the first area, a new technique called two-step saturated fluorescence has been used to detect atomic hydrogen in flames (in point measurements and in two-dimensional images) without the complicating edge effects of other saturation-spectroscopy techniques. An exhaustive experimental comparison has been made of the many multiphoton fluorescence and optogalvanic techniques that can be used to detect atomic hydrogen and oxygen in flames. In the second area, an intracavity-doubled ring dye laser has been used to greatly improve the sensitivity of hydroxyl radical fluorescence probes. Multiphoton nonlinear techniques have been used to develop a hydrogen atom probe for use in kinetics studies. In the third area, collisional narrowing is being modeled both by extensive semiclassical trajectory calculations and by simple scaling theories based on fits to experimental data. Analytic theories have been developed to explain saturation and Stark effects seen in multiphoton nonlinear fluorescence experiments on atomic hydrogen. [3.0 FTE]

72. *Combustion Research Facility (CRF) Central Laser Systems*
R.L. Schmitt, R.L. Farrow, L.A. Rahn, R.E. Palmer

This project includes the continued development of existing CRF central lasers and research in support of future major laser systems. The tunable dye laser (DIANA) is being used by Sandia staff and visiting scientists for single-shot temperature, density, and species concentration measurements and two-dimensional imaging of turbulent nonpremixed flames. A multipurpose laser system (Sirius) consists of a frequency-doubled Nd:YAG laser and several dye laser options including a broadband dye laser and a pulse-amplified ring dye laser. When the Nd:YAG laser is operated in single-axial mode in combination with the ring dye laser, the spectral resolution for CARS and other nonlinear spectroscopy experiments (performed in any of the CRF laboratories via the beam distribution system) is as small as a few thousandths of a wavenumber. Sirius is used frequently for CARS measurements in flames with large luminous backgrounds (e.g., heavily sooting flames or flames laden with coal particles). A third central laser (Dyeblaster) consists of a frequency-doubled Nd:YAG laser and is used routinely to pump dye lasers in user laboratories throughout the CRF. Present laser research in support of advanced central lasers includes diode-laser injection locking of Nd:YAG lasers for stable single-axial-mode operation, and studies of advanced dye laser design. [3.0 FTE]

Atomic Physics

Argonne National Laboratory
Argonne, Illinois 60439

Physics Division **$1,988,000**

73. *Photoionization Mass Spectrometry, Photoelectron Spectroscopy, and Photodissociation*
J. Berkowitz

Fundamental processes in the photoionization of atoms and small molecules are studied in the vacuum ultraviolet at high photon resolution. For molecules, alternative decomposition modes are investigated to provide important thermochemical values, structural, and dynamical information. Photoelectron spectroscopy is focused on the more difficult high-temperature vapor species and reveals their detailed electronic structure. A recently completed apparatus enables us to study directly the spectroscopy and dynamics of molecular-ion decomposition by analyzing the decomposition products from interaction of ultraviolet-laser radiation with selected molecular ions. [3.9 FTE]

74. *Atomic Spectroscopy with Fast Beams at Argonne National Laboratory (ANL)*
H.G. Berry, L. Young

Atomic structure studies using fast-ion beams are aimed principally at improving understanding of relativistic and quantum-electronic effects in heavy ions. Systems with only a few (1 to 4) electrons are studied to test precise *ab initio* calculations; many-electron systems are studied to test more general relativistic calculations (e.g., relativistic Hartree-Fock). In atomic collision studies, the alignment and orientation production of excited states in fast ion–solid interactions are analyzed. Total excitation probabilities are also measured and studied in terms of secondary-electron production and molecular coherence effects. Optical techniques are used to study the dynamics of fast and atomic ions in solids and at surfaces. Resonant laser excitation of fast ions is being used to study (in detail) relativistic fine structures and hyperfine structures of both positive and negative ions of low nuclear charge. Research includes use of lasers operating in the ultraviolet. [4.4 FTE]

75. *Theoretical Atomic Physics*
K.T. Cheng

This project is directed toward a detailed understanding of the role of relativity and electron correlation in atomic processes. Emphasis is on photoexcitation and photoionization to gain important insight into the dynamics of many-electron interaction in atoms and ions. Current efforts include the systematic study of the ground-state hyperfine structures of rare-earth elements using a technique based on the multiconfiguration Dirac-Fock method. The same technique is used to study the fine and hyperfine structures of the Li^- ion, which are very sensitive to Breit interaction and electron correlation effects. Studies also involve the changes in the correlation effect along an isoelectronic sequence as reflected in the profiles of the autoionization resonances. The purpose of this study is to gain better understanding of the dynamics of Rydberg series interactions. [1.1 FTE]

76. *High-Resolution Laser-RF Spectroscopy with Atomic and Molecular Beams*
W.J. Childs, L.S. Goodman

This project is directed toward a detailed understanding of the structure of atoms and small molecules. In the recent past the spin-rotation and hyperfine interactions of alkaline-earth monohalide radicals have been systematically studied and their dependence on vibrational, rotational, and isotopic effects elucidated. The experimental methods have now been extended to make possible measurement of the electric-dipole moments of such radicals. A similar project aimed at a systematic understanding of the hyperfine interaction throughout the 4f-shell of the rare-earth atoms is progressing concurrently. A new apparatus for analogous studies of atomic and molecular ions using collinear laser and radiofrequency spectroscopy is under development. [3.1 FTE]

77. *Interactions of Fast Atomic and Molecular Ions with Solid and Gaseous Targets*
E.P. Kanter, Z. Vager, D.S. Gemmell

Argonne National Laboratory's 4.5-MV Dynamitron accelerator is used to study the interactions of fast (MeV) atomic and molecular ions with matter. A unique feature is the exceptionally high resolution (~0.005° and ~300 eV) in angle and energy obtained in detecting particles emerging from the target. The accelerator currently permits the coincident detection of up to three molecular dissociation fragments with conventional discrete particle detectors. A new multiparticle imaging detector system is currently under development to allow detection of multiparticle events consisting of up to eight particles. The main objective is a general study of the interactions of fast charged particles with matter, emphasizing those aspects that take advantage of the unique features inherent in employing molecular-ion beams (i.e., each molecular ion incident upon a solid target forms a tight cluster of atomic ions that remain correlated in space and time as they penetrate the target). Additionally, these techniques allow direct determination of the geometrical structures of molecular ions entering the target. [4.9 FTE]

Brookhaven National Laboratory
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Applied Science Department **$262,000**

78. *Atomic Physics Research*
K.W. Jones, B.M. Johnson

This project uses synchrotron radiation produced by the Brookhaven National Synchrotron Light Source (NSLS) and heavy-ion beams from the Brookhaven Tandem Accel-Decel Laboratory (TADL). A large, dedicated atomic physics station on a beam line at the NSLS x-ray ring will be used for experiments with white or monochromatic x-rays. The first experiments will be performed with the white beam investigating the production of multiply-charged trapped ions by sequential photoionization. These ions will have very low kinetic energies and will be used for spectroscopic studies or precision collision measurements. Further research will develop instrumentation for crossed photon-ion beam experiments. Work has begun with the use of standard ion sources; the long term aim is to add electron beam ion sources and heavy-ion storage rings to increase capability for study of highly ionized atoms. Ion beams from TADL are used to study various aspects of ion-atom and ion-electron collisions. Energies for negative ions cover the range from about one to nine MeV. Beams of almost fully stripped elements up to iron can be produced with energies from several to several hundred MeV when the tandems are operated in the accel-decel and three-stage configurations. A lesser degree of ionization is obtained for heavier elements. Charge transfer and equilibrium charge states in ion-gas collisions are studied with negative ions, and with positive ions produced by the tandem accel-decel method. Inner-shell vacancy processes are also studied with these beams. [3.0 FTE]

Lawrence Berkeley Laboratory
Berkeley, California 94720

Materials and Molecular Research Division **$245,000**

79. *Atomic Physics at Lawrence Berkeley Laboratory (LBL)*
R. Marrus

This project concerns experimental study of collisions and spectroscopy in simple atomic systems. Emphasis is on those processes pertinent to controlled thermonuclear reaction devices and processes important to fundamental physical laws: (1) electron capture by low-energy multicharged ions; (2) x-ray spectroscopy of helium-like, lithium-like, and beryllium-like ions of high Z; (3) parity violation in heavy atoms predicted by unified theories of weak and electromagnetic interactions; (4) charge capture and loss by fast multicharged atoms in solid and gas targets; and (5) study of quantum electrodynamic effects and relativistic effects in hydrogenic and helium-like uranium. These studies are made possible by use of (1) the SuperHILAC and Bevalac that produce a range of heavy ion beams at energies greater than any other facility in the world and (2) narrow band, high-power ultraviolet lasers developed within the group for studying parity violation in atomic systems. [3.3 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Physics Division **$1,256,000**

80. *Theoretical Atomic Physics at Oak Ridge National Laboratory (ORNL)*
R.L. Becker, C. Bottcher

Theoretical predictions, interpretations of experimental results, and detailed calculations are made for atomic collision, radiation, and structure phenomena. Emphasis is placed on reactions of highly stripped ions with atoms, particularly those reactions of importance in fusion energy devices and those studied in atomic high-energy accelerator physics laboratories. Atomic excitation, ionization, and electron transfer (capture) are treated. Recent activities include calculations of multiple K-, L-, and M-shell vacancy production by ions (being detected in x-ray satellites at the Oak Ridge National Laboratory Holifield heavy ion accelerator), subshell vacancy production including the effects of vacancy rearrangement processes, electron capture and ionization in the nearly symmetric system F^{+9} + Ne at both low and high impact speeds, electron ejection and positron production in collisions of very heavy ions with very heavy atoms, and collisions of ions with atoms containing a highly excited (Rydberg) electron. New theoretical approaches include the one-and-a-half center version of coupled-channels theory, the unification of shakeoff theory with collision theory, and the use of finite elements in the numerical integration of time-dependent quantal equations. Computer programs for solution of the time-dependent many-electron Hartree-Fock and one-electron Dirac equations have been developed in the last year. [1.0 FTE]

81. *Accelerator Atomic Physics*
S. Datz, P.F. Dittner, P.D. Miller

The project objective is to achieve a detailed understanding of the interactions of high-energy, multiply charged, heavy ions with gas, solid, and electron targets. The primary facility used is the EN-tandem accelerator. Ion-ion collisions at low energies are also being investigated, and several experimental programs are continuing on the Holifield accelerators. Subjects receiving particular attention during the past year are: (1) cross-section measurements of dielectronic recombination of several lithium-like, boron-like, and sodium-like ions using a merged multiply charged ion beam concentric with an electron beam; (2) dependence of dielectronic recombination on stripping fields for C^{+3} and B^{+2}; (3) transverse correlation effects on ion channeling trajectories; (4) production of polarized highly stripped ions by electron capture in ferromagnetic crystal channels; (5) mechanisms for transfer ionization; (6) continuing study of positron and electron channeling radiation; and (7) resonant coherent excitation of one electron ions. Results in these areas impinge directly on fusion research, solar corona studies, and material sciences, as well as improving fundamental understanding of ion-atom, ion-solid, ion-ion, and ion-electron interactions. [5.2 FTE]

82. *EN Tandem Operations*
P.D. Miller, P.L. Pepmiller

The EN-tandem Van de Graaff is operated for atomic physics research. Terminal voltages up to 6.0 MV are routinely achieved, and ions of all elements from Z = 1 through 9 and many heavier ions are available for users. The user group includes members of the physics division, other divisions of Oak Ridge National Laboratory, faculty and students from various universities, and representatives from industry. During 1984 and 1985, a new VAX-750/CAMAC-based data acquisition system is being installed. All hardware and software are purchased, and installation will be completed by summer of 1985. The major beam usage during 1983 was for the merged electron heavy ion beams experiments, two electron correlated transfer studies, convoy electron studies, trapping of low energy highly charged ions, and channeling experiments. Approximately 40% of the available beam time was allotted to university users. [1.3 FTE]

83. *Collisions of Low-Energy Multiply Charged Ions*
R.A. Phaneuf, F.W. Meyer

This experimental project is aimed at improving our understanding of inelastic collision processes involving multiply charged ions at the lowest attainable collision energies. The current emphasis is on measurement of total cross sections for electron capture by highly stripped ions from hydrogen atoms at energies below 1 keV/amu. Toward this end, two different experimental approaches are being pursued. The recently-implemented ORNL-ECR ion source is utilized as a source of low-energy, highly stripped ions, which are directed through a calibrated thermal-dissociation atomic hydrogen gas target. Total electron-capture cross sections have been measured recently for bare and hydrogen-like ions of carbon, nitrogen, oxygen, fluorine, and neon at energies as low as 200 eV/amu, and provide data for testing coupled-state theoretical calculations and predicted ionic charge scalings at low energies. An ion-atom merged-beams apparatus is also in final stages of development and testing. This will permit an extension of the study of such collisions to center-of-mass energies in the eV/amu range, where theoretical predictions of increasing cross sections with decreasing energy remain untested. [1.4 FTE]

Sandia National Laboratories
Albuquerque, New Mexico 87185

Laser and Physical Chemistry Department-1124	**$155,000**

84. *Atomic Processes*
A. Owyoung, A.V. Smith

This project focuses on the study of high-order nonlinear optical interactions in atomic and molecular systems; the objective is to uncover an efficient method for the generation of fully tunable coherent vacuum ultraviolet radiation. Present investigations concentrate on two-frequency summing processes in atomic vapors whereby third harmonic generation at one frequency is enhanced by a second laser source, which effectively couples the process into a four photon resonance with the atomic system. We will continue to explore phenomena involving such optically induced structure in the continuum between states, extended out to the ionization continuum. These subsequent studies will extend the accessible vacuum ultraviolet tuning range and provide for the exploration of more complex interactions expected to occur when resonant ionization becomes a significant consideration. This project will provide a new and potentially very useful means for vacuum ultraviolet generation and will contribute significantly to our understanding of the complex interactions of optical radiation with atomic and molecular systems. [1.5 FTE]

Chemical Energy

Ames Laboratory
Ames, Iowa 50011

Processes and Techniques Program	**$962,000**

85. *Organometallic Complexes in Homogeneous Catalysis*
R.J. Angelici

Although sulfur is removed commercially from thiophenes in crude petroleum by hydrodesulfurization (HDS) over sulfided metal catalysts, the mechanistic details of this process are not understood. The purpose of this project is to develop some understanding of the reactivity of thiophene coordinated to transition metals as might occur on the catalyst surface. It has been found that the π-complexed thiophene in $(\eta\text{-}C_4H_4S)Mn(CO)_3^+$ is highly activated to react with metal hydride complexes such as $HFe(CO)_4^-$ and $HW(CO)_5^-$. Reaction with acids leads to the formation of 2,3-dihydrothiophene, a possible intermediate in the HDS process. Reactivity studies of 2,3-dihydrothiophene to determine how sulfur is removed from this molecule are also in progress. These studies are offering new mechanistic pathways by which the HDS process might occur. [2.7 FTE]

86. Chemical Kinetics and Reactivity of Transition Metal Complexes

J.H. Espenson

The primary objective is to provide fundamental data on chemical reactivity bearing on chemical reactions involved in homogeneous catalysis, synthetic fuels, the Fischer-Tropsch process, and the control of acid rain. The principal approach is based on the study of chemical kinetics and of reaction mechanisms using a wide variety of experimental techniques applied to reactions occurring from micro-seconds to days or longer. The reactions under investigation include spontaneous and induced decomposition, heterolytic and homolytic metal–carbon bond cleavage (and the associated bond-dissociation energies), radical-induced electron transfer, free radical displacement, alkyl transfer, and insertion into metal-metal and metal–carbon bonds. The chemical entities under study include organometallic derivatives of cobalt, chromium, nickel, and rhodium; dinuclear complexes of platinum, nitrogen oxides, and oxoacids; sulfur dioxide; and molecular elements (e.g., S_8 and P_4). [4.9 FTE]

87. Nuclear Magnetic Resonance (NMR) Studies of Coals, Catalysts, and Amorphous Semi-Conductors

B.C. Gerstein

Nuclear spin dynamics are used to probe the physics and chemistry of materials involved in heterogeneous catalysis, coals and coal products, and materials science. Examples include precursor pitches used in electrodes for aluminum production, zeolitic catalysts used in conversion of methanol to ethylene, bimetallic catalysts, heavy metal halide cluster compounds, and amorphous semiconductors used in photoconversion. [4.0 FTE]

88. Spectroscopic and Kinetic Characterization of Metal Oxide and Sulfide Catalysts

G.L. Schrader

The goal of this research is to develop a fundamental understanding of the solid-state and surface chemistry of heterogeneous catalysts and the mechanisms of catalytic reactions. Metal oxide and sulfide catalysts used industrially to produce synthetic fuels or to hydrotreat coal-derived liquids are being investigated. Catalysts for energy-efficient routes to chemicals are also included in this research. Spectroscopic techniques such as laser Raman spectroscopy and Fourier transform infrared spectroscopy are being developed for use in the characterization of catalysts and adsorbed species. *In situ* experiments are being performed involving functioning catalysts; simultaneous spectroscopic and kinetic measurements can be performed at the temperatures and pressures typical of industrial operating conditions. These techniques provide a direct method for relating catalyst structure and composition to activity and selectivity. Kinetic studies are being performed in this research using pulsed and steady-state fixed bed reactors. [1.9 FTE]

89. High-Temperature Gas-Phase Pyrolysis of Organic Compounds

W.S. Trahanovsky

This research aims at understanding the fundamental thermal reactions of organic compounds, especially those that could be important in the pyrolysis of coal and coal-derived liquids. Study includes (1) preparation of specific reactive molecules thought to be intermediates in pyrolysis reactions and investigation of their spectroscopic and chemical characteristics and (2) reactions thought to involve certain reactive molecules as intermediates. Most pyrolyses are carried out using the flash vacuum pyrolysis technique. Much of the work concentrates on (1) pyrolysis reactions thought to involve quinodimethanes as intermediates, (2) preparing and characterizing these and related species, and (3) thermal reactions of these species and products derived from them. Specific reactive molecules under study include orthoquinodimethanes derived from benzenes, naphthalenes, furans, and thiophenes. [2.2 FTE]

Argonne National Laboratory
Argonne, Illinois 60439

Chemical Technology Division **$491,000**

90. Fluid Catalysis

J.W. Rathke, M.J. Chen, R.J. Klingler, J.J. Heiberger

This research will determine reaction mechanisms and the exploration of new catalytic chemistry for converting small molecules (e.g., CO, CO_2, and O_2) to desired products. Currently under investigation are the roles of soluble metal oxides in promoting the formation of methanol from carbon monoxide and water, and from carbon monoxide or carbon dioxide and hydrogen. The mechanism for soluble oxide catalysis of a new reaction converting carbon monoxide and methanol to formaldehyde is also studied. In each case, the metal oxide chemistry involves coordinated formate ion as a key intermediate and is unusually general in that it often applies to homogeneous, heterogeneous, main group, and transition metal systems. An attempt is also made to advance the chemistry of oxygen carriers for potential use in air separation and controlled oxidation processes. The mechanisms of the reactions are investigated using high-pressure kinetic techniques in addition to spectroscopic and theoretical (molecular orbital) methods. [4.7 FTE]

Chemistry Division **$2,003,000**

91. Inorganic Fluorine Chemistry

E.H. Appelman, L. Stein

This project has a twofold objective: (1) synthesis and characterization of novel and aggressive oxidants and fluorinating agents, elucidation of the mechanisms of their chemical reactions, and development of applications of these compounds to actinide research and other areas of chemistry; and (2) study of the chemistry of radon. Activities include (1) studies of hypofluorites and other fluorinating reagents in low-temperature matrices, (2) preparation of new hypofluorites, (3) investigation of the reactions of fluorine and reactive fluorine compounds with aqueous solutions, and (4) use of reactive fluorinating agents as specific reagents for the preparation of high oxidation states of actinide elements and selectively fluorinated organic compounds. Work in the area of radon chemistry involves (1) studies of the behavior of oxidized radon in a variety of solvents and a search for new benchtop solvents for radon compounds, (2) studies of the absorption of oxidized radon onto several oxidation-resistant ion-exchange materials, (3) a search for compounds of radon with oxygen and with halogens heavier than fluorine, and (4) efforts to develop improved chemical methods for the analysis of radon. [2.1 FTE]

92. *Premium Coal Sample Program*
K.S. Vorres

The objective of this program is to provide the U.S. basic coal science research community with long-term supplies of a small number of premium coal samples. The premium coal samples produced and distributed by this program are to be as chemically and physically identical as possible, have well-characterized chemical and physical properties, and must be stable over long periods of time. Coals are to be mined, transported, processed into desired particle and sample sizes, and packaged in environments that are as free of oxygen as possible and that maintain the natural moisture content to ensure that the coals are kept in as pristine and stable condition as possible. These premium samples are to be distributed to researchers upon request. It is anticipated that a computer data base will be included in this program to provide researchers with easy access to detailed information on sample availability, the physical and chemical properties of the coals, and references to the results of research obtained using these samples. [3.0 FTE]

93. *Separation of Coal Macerals*
R.E. Winans, G.R. Dyrkacz, C.A.A. Bloomquist

The project seeks to reduce the complexity of coal science by developing new methods for separating and characterizing coal macerals. The density gradient centrifugation technique developed in this study has provided pure maceral samples for fundamental coal research and samples for the explanation of coal maceral characteristics, which could lead to improved separation methods. Focus is on investigating surface properties of macerals using radiolabeling, proton NMR, and microcalorimetry to provide improved separation methods. [3.4 FTE]

94. *Characterization and Reactivity of Coals and Coal Macerals*
R.E. Winans, R. Hayatsu, R.E. Botto, R.G. Scott, R.M. McBeth

The major objective of this project is to identify important organic structural components in coals and coal macerals and to correlate this information with the chemical and thermal reactivity of these materials. Coal macerals are being characterized by a combination of chemical and instrumental techniques. Realistic coal models are being synthesized from presumed coal precursors, which yields information on coal formation and its structure. Techniques such as solid NMR, pyrolysis, and fast bombardment mass spectrometry, along with selective chemical reactions, are being used to study the macromolecules in coal macerals. Information obtained in this study should ultimately help develop more efficient and cleaner ways to use coal. [7.2 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Applied Science Department $667,000

95. *High Temperature Chemistry*
J.J. Egan

This study of the thermodynamic and transport properties of inorganic substances at high temperatures attempts to explain the results in terms of appropriate atomic models. Substances include solid and liquid compound semiconductors, solid electrolytes, and molten salts. Electrochemical techniques are used to investigate the effect of composition on the concentration, mobility, and diffusion of electrons and electron holes in these substances. Cells employing solid electrolytes at high temperatures as well as molten salt electrolytes prove especially useful for characterizing these systems. High temperature calorimetry is being used to study liquid semiconductors and other liquid alloy systems. Molten salts are studied since they are important for the development of high energy-density batteries and fuel cells. The electronic conductivity of these melts in particular is examined by special techniques. Solid compound semiconductors of potential use as solar cells are studied by high temperature electrochemical techniques. [2.2 FTE]

96. *Metal Hydrides*
J.J. Reilly

This project focuses on determining the thermodynamic properties and structural parameters of metal alloy-hydrogen systems. Specific goals are (1) to relate hydriding properties of metal alloys to their structure and composition, (2) to determine alloy-hydrogen phase diagrams, (3) to determine and systematize crystal structure, and (4) to relate all pertinent data and observations to predict the behavior of a given alloy-hydrogen system. Current topics of interest are the causes of the observed deviations from ideal behavior of certain intermetallic-hydrogen systems, surface and near surface properties of metal-hydrogen systems, structure of metal hydride phases, the influence of defects upon system behavior, and reaction kinetics of metal hydride suspensions. Major experimental tools and/or techniques are x-ray and neutron diffraction, equilibrium pressure temperature composition measurements, ion beam analysis, and magnetic susceptibility measurements. [4.1 FTE]

Chemistry Department $205,000

97. *Organometallics in Homogeneous Catalysis*
M.A. Andrews, R.M. Bullock

This project clarifies the role that soluble transition metal complexes can have in the homogeneous catalytic activation of organic or small molecule substrates. Potential long term goals include the discovery of more efficient catalysts and the development of new insights into the mechanisms of both homogeneously and heterogeneously catalyzed processes. A specific example is the transition metal-catalyzed reaction of olefins with H_2 and CO to form aldehydes (the hydroformylation reaction). Evidence for the importance of radical pathways in this reaction will be sought by studying the reactions of a series of metal hydrides of the type $HM(CO)_n$ with suitably chosen olefins. Another example is the reaction of metal hydrides with metal alkynyl complexes to form either dimetalla alkenes or bridging vinylidene complexes. A series of metal hydrides of known acidity will be investigated to test the relative importance of proton and hydride transfer reactions in this system. [6.1 FTE]

98. Mechanisms of Photo-, Enzyme-, and Chemically Catalyzed Cis-Trans Isomerization

S. Seltzer

Cis-trans isomerization can be brought about by the application of heat or light, or by catalysts. Because the physical and chemical properties of the two isomers differ, relaxation of a non-equilibrium mixture of isomers (achieved by irradiation) to the equilibrium mixture can result in the release of thermal or electrical energy. This cis-trans energy-producing effect is utilized in biological processes such as vision in animals and the light-driven proton pump of Halobacteria, which can be used in a photogalvanic cell. Studies at Brookhaven National Laboratory are concerned with mechanisms of cis-trans isomerization catalyzed by chemical reagents, by enzymes, and by light, and their applications to the mechanism of the bacteriorhodopsin proton pump. [1.5 FTE]

Lawrence Berkeley Laboratory
Berkeley, California 94720

Materials and Molecular Research Division **$1,117,000**

99. High Energy Oxidizers and Delocalized-Electron Solids

N. Bartlett

The project objective is synthesis and characterization of new materials that may have value in electrochemical applications. The synthetic work examines models and theories that correlate physical properties (e.g., electrical conductivity) with chemical composition and structure. Present emphasis is on the study of two-dimensional extended-atomic networks such as those derived from graphite, layer-form boron nitride, and their relatives. Electron oxidation of such materials (with accompanying intercalation to form salts) generates durable and conductive materials (some conducting better than aluminum). Chemical, stoichiometric, and structural requirements for the best conductivity are being defined. The layered materials can often be oxidized (and intercalated) electrochemically in a reversible process. Some of these materials (e.g., $C_xF_{-1}\delta$, δ HF) may be useful for high energy electrodes. Physical and chemical studies are being applied to such materials to determine the structure and bonding changes that accompany oxidation and reduction. Salts that are either proton conductors or fluoride-ion conductors, and are resistant to oxidation but not metallic, are being sought as solid electrolytes for use with metallic layer-material salts. [4.0 FTE]

100. Catalytic Hydrogenation of Carbon Monoxide

A.T. Bell, G.A. Somorjai

The purpose of this project is to develop an understanding of the fundamental processes involved in catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Focus is on defining the factors that limit catalyst activity, selectivity, and resistance to poisoning, and the relationship between catalyst composition/structure and performance. A variety of surface diagnostic techniques (LEED, AES, XPS, EELS, IRS, TPD) are used to characterize supported and unsupported catalysts before, during, and after reaction. The information thus obtained is combined with detailed studies of reaction kinetics to elucidate reaction mechanisms, and the influence of modifications in catalyst composition and/or structure on the elementary reactions involved in carbon monoxide hydrogenation. [6.5 FTE]

101. Transition Metal Catalyzed Conversion of CO, NO, H_2, and Organic Molecules to Fuels and Petrochemicals

R.G. Bergman

The main objective of this project is the discovery of new chemical reactions between organic compounds and transition metals, and the understanding of how these reactions work. Particular attention is paid to transformations that involve the most fundamental bonding changes (e.g., formation and cleavage of bonds between carbon, hydrogen, nitrogen, and oxygen), and that occur in important large-scale transformations of organic compounds, such as those employed in industrial catalysis and stoichiometric organic synthesis. A recent project discovery was that a certain class of iridium complexes undergoes oxidative addition into the carbon-hydrogen bonds of completely saturated hydrocarbons (alkanes). This is the first example of this long sought carbon-hydrogen activation reaction, and recent research aims at understanding its scope and selectivity. Recently, methods for extending the iridium-based alkane activation chemistry to appropriately substituted rhodium complexes have been developed. Work is underway to study the properties of these different metal systems, understanding and comparing the mechanisms of the reactions, and developing methods for using this chemistry to convert alkanes into more useful, functionalized organic molecules. [4.5 FTE]

102. Formation of Oxyacids of Sulfur from SO_2

R.E. Connick

The research is aimed at understanding (1) the fundamental chemistry of sulfur species formed from sulfur dioxide in aqueous solution and (2) the chemical reactions of these species. The chemistry of these systems is of particular importance in the problems associated with atmospheric pollution by sulfur dioxide and the resulting formation of acid rain. Research has focused on the kinetics of the exchange of oxygen atoms between bisulfite ion and water, using the nuclear magnetic resonance of ^{17}O to follow the reaction. Results indicate a rate law consistent with exchange through formation of sulfur dioxide. Future work will be directed to the kinetics and mechanisms of oxidation-reduction reactions of sulfur(IV). A secondary and not closely related goal is to determine the factors controlling the rate of substitution reactions in the first coordination sphere of metal ions. Computer modeling of such systems is underway and some results for a two-dimensional model have been published. Work will be extended to three dimensions using a more sophisticated model for water. Nuclear magnetic resonance measurements of water exchange from partially complexed metal ions are also being made using ^{17}O. [1.0 FTE]

103. Synthetic and Physical Chemistry

W.L. Jolly

The main objective of this project is to determine the nature of the chemical bonding in transition-metal organometallic complexes related to catalytic systems. The experimental tool is gas-phase x-ray photoelectron spectroscopy, which provides atomic core electron binding energies. The binding energies give information about the distribution of valence electron density and the nature of the chemical bonding in the molecules. By measuring the core binding energies of appropriate transition metal compounds, it is possible to study the interaction of metal d electrons with various ligands (e.g. organic groups, carbonyl groups, and nitrosyl groups). One can identify and distinguish various modes of ligand-metal bonding that have analogs in the molecules chemisorbed on metal surfaces and in the intermediates of catalyzed organic reactions. Of particular interest are studies of metal cluster complexes, in which the ligand-metal interactions are very similar to those on metal surfaces. [1L1.5 FTE]

104. Surface Chemistry: Application of Coordination Principles

N.E. Phillips

The project objective is to define the coordination chemistry of transition metal surfaces on a comparative basis with that of molecular metal complexes and molecular metal clusters. Displacement reactions supplemented with diffraction and spectroscopic data will be used to elucidate structural, bonding, and chemical features of the nickel and platinum metal surfaces with chemisorbed molecules. Initial studies focused on the chemisorption states of aromatic hydrocarbons, olefins, and acetylenes on nickel and platinum surfaces. Catalytic reactions of these molecules will be examined in an ultrahigh vacuum chamber equipped with an isolation cell. These catalytic reactions will be closely correlated with metal cluster research to obtain a precise comparison between homogeneous and heterogeneous catalysis. Theoretical analysis, based on symmetry matching of energetically available metal surface orbitals with those of molecules and molecular fragments of hydrocarbons, has been developed for a further comparison with structural data. [1.8 FTE]

105. Organometallic Chemistry of Coal Conversion

K.P.C. Vollhardt

The project objective is to design and synthesize novel organometallic compounds that will exhibit new properties as potential catalysts in reactions to be used in conversion of coal to liquid and gaseous fuels. The specific aim is to construct new molecules that may activate organic chemicals to new reactions and (by virtue of their unusual topology and/or electronic make-up) be important new materials (e.g., photostorage devices, photocatalysts, conductors). Recent work has centered on the novel and unusual chemistry of fulvalene dimetals, which has led to the discovery of unprecedented binuclear chemistry of homo- and heteronuclear transition metal derivatives. Several of these compounds have shown novel and distinct chemistry of relevance to catalysis, surface reactions, and photochemical storage cycles. Work on fulvalene dimolybdenum, tungsten, and ruthenium has uncovered new binuclear modes of hydrogen evolution from dihydrides, carbon-carbon bond formation through biscarbenes, and the occurrence of unprecedented mechanisms of photosubstitution; and has led to the use of photochemically activated complexes in thermal chemical processes, the observation of stepwise carbon monoxide reduction, and unusual stereospecificity in degenerate rearrangements. [2.5 FTE]

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Isotope and Nuclear Chemistry Division **$247,000**

106. Labile SO_2 Complexes

G.J. Kubas, R.R. Ryan

Atmospheric pollution by sulfur dioxide and acid precipitation have emerged as major environmental problems. Our research aims at developing regenerative methods for scavenging SO_2 from waste gases either directly or by conversion into less harmful species. Work includes: (1) synthesis and structural characterization of new transition metal complexes of SO_2 and related species such as SO_2H and S_2O_4; and (2) studies of the reactivity of SO_2 coordinated to metal complexes to promote catalytic reactions of SO_2 with other abundant small molecules. The first example of homogeneously catalyzed reduction of SO_2 by hydrogen has been discovered, and products and reaction mechanisms are being studied. Catalysts are organometallic molybdenum sulfide complexes. The use of low cost heterogeneous molybdenum sulfide catalysts (e.g., those used in hydrodesulfurization) is being investigated. Alternatives to using hydrogen as the feedstock reductant are also being explored. Reactions of SO_2 with transition metal hydride complexes are being studied in order to identify intermediates and mechanisms involved in hydrogen transfer to SO_2. We have discovered the first examples of insertion of SO_2 into metal-hydride bonds to form novel SO_2H complexes. This area is being investigated further as a possible key step in hydrogenation. [1.5 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Chemical Technology Division **$350,000**

107. Kinetics of Enzyme Catalyzed Processes

E. Greenbaum, J. Woodward

This project focuses on the physicochemical mechanisms of artificial photosynthetic systems including (1) the reconstituted *in vitro* system composed of isolated spinach chloroplasts, ferredoxin, and hydrogenase (CFH) and (2) the substituted systems in which non-biological catalysts are electronically linked to water splitting and chloroplast-reducing power. Research on the fundamentals of stabilization and immobilization of cellulase is also being performed. Colloidal platinum has been prepared and precipitated directly onto chloroplast photosynthetic membranes. This system is capable of the simultaneous photoevolution of hydrogen and oxygen. Aspects of this result include: (1) this two-component system is among the simplest yet devised for photosynthetically splitting water into molecular hydrogen and oxygen; (2) it eliminates the need for an electron relay (e.g., ferredoxin or methyl viologen) between the oxygen-evolving chloroplasts and the hydrogen-evolving catalyst; and (3) it demonstrates direct interaction of a nonbiological catalyst on a biological membrane with preservation of functional electron transfer between the biological and nonbiological components. In addition, we have shown that manganese divalent cations stimulate the photoevolution of oxygen and hydrogen evolution by the CFH system. Immobilization of cellulose onto a support material with affinity for cellulase (e.g., concanavalin

A-Sepharose) has been shown to be useful for enzyme recovery. [3.0 FTE]

Chemistry Division **$2,302,000**

108. Organic Chemistry and the Chemistry of Fossil Fuels

A.C. Buchanan, B.M. Benjamin, L.L. Brown, E.W. Hagaman, R.R. Chambers

The project objective is a better understanding of the chemical structure and reactivity of coal by developing and applying chemical and spectroscopic techniques to coal. Results will be interpreted by parallel studies with appropriate model compounds. Selective diagnostic reactions for structural features in coal are being developed. Acid-catalyzed transalkylation is being applied to several coals of varying rank; the results allow for quantitative comparison of aliphatic substituents and linking groups. The selective generation and derivatization of coal carbanions based on differences in acidity of C–H bonds is providing new quantitative information on the chemical environment of benzylic C–H bonds in coal. Thermal reaction mechanisms relevant to the thermal decomposition of coal focus on unraveling the modification of free radical reaction pathways resulting from their immobilization on surfaces. Solid-state CP/MAS-^{13}C-NMR experiments are assessing the quantitative aspects of the technique applied to coal and have led to the development of a new internal standard method. NMR experiments are also being performed to assess the feasibility of applying double cross polarization methods to selectively modified coals. [7.8 FTE]

109. Basic Aqueous Chemistry to High Temperatures and Pressures

R.E. Mesmer, H.F. Holmes, W.L. Marshall, D.A. Palmer, J.M. Simonson

The aim of this project is to establish the basic principles that determine the chemical and thermodynamic behavior of aqueous solutions at high temperatures and pressures. The thermodynamic properties of single and mixed electrolytes and nonelectrolytes (including water itself), the dynamics and equilibria involved in the interactions between electrolytes, between dissolved solutes and water, and between solid or gas phases and water are the essence of the chemistry studied within the framework of this project. Progress is dependent on the parallel development and adaptation of a range of diverse, but complementary, experimental techniques to provide precise data at near critical and in some instances, supercritical conditions. New efforts are focused on obtaining structural and detailed molecular information by designing high temperature cells for Raman spectroscopic and neutron scattering experiments in order to broaden the scope of the project. The results of such studies are applicable to steam generation, fuel reprocessing, metal refining, and the disposal of waste, as well as to the extraction of heat and materials from natural resources. These results also provide the opportunity to test and develop new theories for the behavior of solutions at high temperatures. [5.3 FTE]

110. Heterogeneous Catalysis Related to Energy Systems

S.H. Overbury, D.R. Huntley

This project involves two related activities. In the first, the technique of low-energy ion scattering as a surface specific structural tool is being developed and applied to the study of clean and adsorbate covered surfaces of catalytic interest. Comparison of the experimentally observed energy and angle dependencies of the scattered ions with computer simulations allows for quantitative descriptions of surface structure. The information content from alkali metal ions (Li^+, K^+) exceeds that from inert gas ions because of their lower neutralization probability. These methods have been applied to study surface reconstruction of gold(110), bonding geometry and ordering of oxygen, carbon, nitrogen, and sulfur overlayers on molybdenum(001) and molybdenum(111), and surface structure of amorphous $Fe_{80}B_{20}$ ribbon. The second activity, now in the equipment building stage, will examine surface adsorption on metal sulfide surfaces in ultrahigh vacuum by electron energy loss spectroscopy and by thermal desorption spectroscopy. A sample transfer system will permit the sample to be moved to an adjoining high pressure cell, which will be used for monitoring hydrodesulfurization and hydrogenation reactions over a wide pressure range. Measured reactivity and selectivity will be correlated with changes in the surface modified by introducing structural defects, bulk or surface impurities, or changes in stoichiometry. [2.3 FTE]

111. Molten Salt Catalysts for Clean Fuel Synthesis

G.P. Smith, A.S. Dworkin, S.P. Zingg, R.M. Pagni

This research investigates molten salts (1) as catalytic reaction media for organic substrates and (2) as media for characterizing reactive cationic intermediates. Molten salts currently under study are those based on (1) $SbCl_3$ (a weak Lewis acid), (2) Ga_2Cl_6 and Ga_2Br_6 (strong Lewis acids), and (3) Al_2Cl_6 and Al_2Br_6 (Lewis superacids). In the molten state the trihalides of antimony and gallium have a pronounced redox functionality. Instrumental techniques used to study reactions as they occur in the molten state include ESR, NMR, optical spectroscopy, and electroanalytical and spectroelectrochemical procedures. [3.3 FTE]

Pacific Northwest Laboratory
Richland, Washington 99352

Chemical Technology Department **$528,000**

112. Hydrogenation Mechanisms of Coal

J.A. Franz, M.S. Alnajjar, D.M. Camaioni

This project focuses on determining the energetics and mechanisms of free radical reactions related to thermal dissolution of coal in hydrogen donor media. Relative rates of radical rearrangements, atom transfer reactions, fragmentation reactions, and charge transfer reactions are being determined; absolute rates are determined by kinetic laserflash spectroscopy for key atom transfer reactions. The cyclization of o-allylbenzyl radical to 2-indanylmethyl radical, for example, is used as an intramolecular free radical clock to compare atom transfer rates to benzylic radicals, thereby determining the relative donor strength of a wide variety of coal-related donors. Carbon–sulfur bond-making and -breaking reactions and sulfur-centered radical intermediates are being studied. [3.3 FTE]

113. Thermochemical Conversion of Solid Wastes into Liquid Fuels
D.A. Nelson, P.M. Molton, R.T. Hallen

The purpose of this project is to determine the reaction mechanisms involved in biomass liquefaction in aqueous media at elevated temperatures. Due to the complexity and variability of the composition of biomass, the liquefaction of individual biomass components and model compounds is under study. Fast heating and cooling during liquefaction has helped determine the initially formed products. For instance, 3-methyl-2-cyclopenten-1-one, a product from cellulosic materials, is formed from 2,5-hexanedione via an aldol condensation. Several cyclopentenone derivatives formed during cellulose liquefaction are being independently synthesized from substituted 2,4-hexanediones. Examination of these precursors will clarify the route of their formation from deoxysaccharides. Several potential precursor deoxysaccharides, such as 1-hydroxy-2,5-hexanedione, are also being prepared from 5-substituted-2-furaldehyde. Initial results using steam-exploded lignin indicate that the product distribution is similar with both aqueous pyrolysis and alkaline liquefaction procedures. Several model lignin compounds containing β-0-4-alkylarylether and diolether groups were prepared. Model compounds containing guaiacolyl substitution are also being prepared. The liquefaction of lignin components will be examined to determine if phenol-quinone tautomerization is the rate determining step. [1.8 FTE]

Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania 15236

Division of Coal Science **$87,000**

114. Vibrational Spectroscopic Studies of Coal Conversion Catalysts
J.M. Stencel

Recent research has concentrated on understanding nickel-molybdenum and nickel-tungsten interactions in Ni-Mo/Al_2O_3 and Ni-W/Al_2O_3 catalysts. Raman spectroscopy is the primary tool used to define molecular speciation for catalysts in which molybdenum, tungsten, and nickel concentrations have been varied systematically. Additional information concerning the influence of nickel concentration and symmetry of the metal oxide on the Ni-Mo and Ni-W interactions is obtained by *in situ* experimentation and by adsorption of ligand-forming and hydrogen-bonding molecules. Raman experimentation is supplemented by data from other bulk and surface sensitive techniques (e.g., x-ray diffraction, x-ray photoelectron spectroscopy, and ion scattering spectrometry). Correlations of structural and chemical factors associated with the promotional effect of nickel are investigated. The study of oxide catalysts for selective conversion of hydrocarbons and for selective Fischer-Tropsch conversion of CO + H_2 will also be initiated. [1.0 FTE]

Sandia National Laboratories
Albuquerque, New Mexico 87185

Condensed Matter Research Department-1130 **$268,000**

115. Reaction Kinetics Over Single Crystal Catalysts
D.W. Goodman

The goal of this research is to develop an understanding of surface catalyzed reactions at the molecular level using the full complement of modern surface analytical techniques. Of primary importance are those reactions relating to the synthesis of hydrocarbons from H_2 and CO. The experimental work includes the determination of reaction kinetics of hydrocarbon formation and rearrangement over single crystal catalysts. The work is carried out in a custom-built ultrahigh vacuum apparatus allowing both kinetic measurements and surface analysis. Recent studies have addressed the mechanism by which poisons and promoters alter catalytic activity and selectivity as well as the metal site requirements for catalytic activity. These measurements have utilized careful dosing of impurity atoms, either electronegative (e.g., sulfur), neutral (e.g., silver, copper), or electropositive (e.g., potassium), onto a catalytically active single crystal substrate (e.g., nickel, ruthenium, rhodium). These studies have established a relationship between the electronic nature of the impurity atom and its ability to alter the catalytic activity of the substrate for certain reactions. These reactions include CO and CO_2 methanation, oxidation alkane hydrogenolysis, olefin hydrogenation, and alkane dehydrogenation. [1.6 FTE]

Surface Chemistry and Analysis Division-1823 **$100,000**

116. FTIR Catalyst Studies
D.M. Haaland

Fourier transform infrared spectroscopy (FT-IR) is being used to study surface catalyzed reactions over supported metal catalysts. In particular, the reaction of hydrogen and carbon monoxide to form methane and higher hydrocarbons is of interest. Infrared spectroscopy allows the reactant molecules on the surface to be used as effective probes of the local environment to determine modifier-adsorbate, adsorbate-adsorbate, and metal-adsorbate interactions. Therefore, FT-IR can be used to investigate the role of modifiers (promoters and poisons) on both the adsorbed reactants and the kinetics of their reaction to form methane and higher hydrocarbons. The presence or absence of long-range interactions between modifiers and adsorbants will be determined. In addition, FT-IR coupled with temperature programmed desorption and temperature programmed reaction will be used to measure relative strengths of adsorption, rates of reaction, and reaction products formed on catalysts both with and without surface modifiers. [0.5 FTE]

Solar Energy Research Institute
Golden, Colorado 80401

Solar Fuels and Chemicals Research Division $214,000

117. Mediated Electrochemical Reduction of CO_2
D.L. DuBois

This research involves the synthesis and characterization of metal phosphine complexes for evaluation as catalysts for the electrochemical reduction of CO_2, and includes structural, spectroscopic, and electrochemical studies of the metal complexes. The project objective is to elucidate factors important in promoting (1) reversible two-electron redox processes and (2) electrochemical reduction of CO_2. Incorporation of these complexes into polymers is being studied for the purpose of developing electrocatalytic modified electrodes. A number of analytical techniques are being used to characterize these polymers in both oxidized and reduced forms. These techniques include cyclic voltammetry, infrared spectroscopy, UV-VIS spectroscopy, and ^{31}P NMR spectroscopy. *In situ* spectroelectrochemical studies of the modified electrodes are possible in favorable cases. [0.5 FTE]

118. Basic Research in Synthesis and Catalysis
J.C. Smart, C.J. Curtis

This basic research project involves the synthesis, characterization, and reaction studies of transition metal coordination complexes and organometallic compounds for the photoconversion of N_2, CO, CO_2, H_2O, and related substrates to fuels and chemicals. It includes structural, spectroscopic, and mechanistic studies with the goal of understanding the interrelationship of molecular geometry, electronic structure, and catalytic reactivity in photochemical and photoelectrochemical transformations. Designed organometallic synthesis has yielded new bi- and trimetallic complexes with bridging fulvalene, *s*- and *as-indacene,* and trindene ligands of titanium, zirconium, tantalum, molybdenum, and manganese. Reactions of CO with early transition metal hydride complexes are being studied in an effort to develop H_2/CO catalysts. Spectroscopic and photochemical studies of cobalt and nickel metallofulvalene and metalloindacene complexes are contributing to an understanding of their electronic structures and the potential utility of their low-lying excited states in photocatalysis. [1.5 FTE]

Separation and Analysis

Ames Laboratory
Ames, Iowa 50011

Processes and Techniques Program $1,008,000

119. Analytical Spectroscopy
V.A. Fassel

This project entails systematic observation of spectroscopic phenomena in order to derive new spectroscopic analytical concepts that offer promise of solving singularly difficult analytical problems in the various fields of energy generation (e.g., conversion of coal to liquid and gaseous fuels, recovery of shale oil, solid state materials research, and environmental pollution assessment). Emphasis is on: (1) novel applications of electrical plasmas as vaporization-atomization-excitation-ionization sources for analytical atomic emisssion, mass, and fluorescence spectrocopy; (2) analytical applications of highly selective energy transfer from energetic, long-lived species to trace level organic or inorganic constituents leading to optical emission; (3) use of processes developed in (2) to devise noble-gas afterglow, GC or LC detectors for element specific, multielement speciation at trace concentration levels; and (4) photoacoustic and thermal wave imaging processes and their analytical applications. [4.7 FTE]

120. Analytical Separations and Chemical Analysis
J.S. Fritz

A major effort is underway to improve our new method of ion chromatography, so that complex mixtures of inorganic anions and cations can be separated and analyzed with the same facility that is possible in organic chromatography. Research on ion-exchange resins is designed to provide better resins for chromatography and to give a better understanding of the important scientific problem of resin selectivity. New methods are being developed for the selective concentration of various organic compounds prior to chromatographic analysis. Improved statistical theories of chromatography are being formulated to correct some inadequacies of prevailing theories and thus provide a better foundation for chromatography. [2.2 FTE]

121. Mass Spectroscopy in Chemical Analysis
R.S. Houk

The general objective of this research project is to develop, evaluate, and characterize ionization techniques with potential value for analytical mass spectrometry (MS). Current efforts concentrate on improving techniques for extracting and mass analyzing ions from inductively coupled plasmas (ICPs). The value of this ion source for elemental and isotopic analysis of solutions on a rapid, direct basis is being demonstrated. Various alternate techniques for introducing samples are being studied with the ICP-MS device as an element-selective, isotopically-sensitive detector. These sample introduction methods include electrothermal furnaces or arc discharges for direct vaporization of solids and liquid chromatographic separations for determining elemental speciation via isotopic tracing experiments. Mass spectra of polar, nonvolatile organic compounds can be obtained directly from aqueous solutions provided ICP conditions are properly cooled. Temperatures, ion and electron densities, and energy transfer processes in ICP are being modeled and studied experimentally. Ionization techniques for mass spectrometric analysis of solids are also being investigated. These techniques include a laser probe for direct, absolute elemental analysis and a pulsed neutral atom beam for desorption and ionization of nonvolatile organic molecules. [2.4 FTE]

122. Lasers in Analytical Chemistry
E.S. Yeung

This project will develop new analytical techniques relevant to pollution monitoring, combustion diagnosis, and material evaluation in energy production. New spectroscopic concepts and instrumentation (particularly those involving lasers) are studied so that analytical methods can gain in sensitivity, selectivity, accuracy, and speed. Focus is on: (1) the development of the laser microprobe for atomic spectroscopy on surfaces; (2) new optical detectors for liquid chromatography suitable for complex organic samples; (3) nonlinear Raman methods and two-photon methods applied to analytical problems; (4) photoacoustic and interferometric concepts for improved absorption measurements, especially in flow systems; (5) high resolution spectroscopy for stable isotope ratio determinations; and (6) laser-induced chemiluminescence for specific gas analysis. Investigations include the fundamental principles behind the measurements, evaluation of the analytical potentials, and demonstration of the analytical method in representative samples. [6.0 FTE]

Argonne National Laboratory
Argonne, Illinois 60439

Chemistry Division $960,000

123. Separations Science Related to Nuclear and Hydrometallurgical Technology

E.P. Horwitz, P.R. Danesi, H. Diamond, D. Kalina, L. Kaplan

The project objectives are (1) development of new separation processes and energy-efficient techniques applicable to nuclear and hydrometallurgical technologies and (2) elucidation of the basic chemistry involved. Major areas of investigation are: (1) the synthesis and characterization of new extractants for metal ion separation by liquid-liquid extraction (LLE) and supported liquid membranes (SLM); (2) the basic physical chemistry of supported liquid membranes, emphasizing various factors that influence the permeability rates of metal ions; and (3) the evaluation of the separation potential of new extractant and SLM systems, with emphasis on developing new methods for by-product recovery from radioactive waste, energy-efficient techniques for the recovery of critical and strategic materials from low-grade domestic sources, and new methods for processing radioactive waste streams. [8.1 FTE]

124. Study of Atmospheric Trace Gases by Mass Spectrometry

C. Stevens

The carbon isotopic compositions of atmospheric methane and natural and anthropogenic sources of methane are being measured to establish the relative distribution of these sources. In addition, we are collaborating with Dr. R. Rasmussen of the Oregon Graduate Center in analyzing the isotopic composition of methane in old air samples collected in both hemispheres since 1978. Changes in the composition reflect changes in the fluxes of enriched or depleted ^{13}C–methane. The purpose of these measurements is to provide clues for causes of an increasing concentration of atmospheric methane, whether it is caused by increasing source fluxes or a decreasing rate of removal from the atmosphere. The results of this study bear on the extent of the methane contribution to the so-called greenhouse effect and its effect on future climate changes. They also provide important quantitative knowledge of anthropogenic source fluxes of CH_4 and the global concentration of atmospheric OH radicals. [0.4 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Applied Science Department $590,000

125. Specific Molecular Property Detectors for Chromatographic Analysis

J.S. Gaffney, E.T. Premuzic

We are developing novel specific molecular property detectors for use in gas and liquid chromatography. Detection schemes are devised that simplify the separation analyses by increasing the detector response for the specific molecules of interest while reducing the background noise from potential interferences. Areas of application range from process monitoring to trace analysis in organic geochemistry, environmental, and biomedical investigations. The project is currently developing monitoring devices for specific hydrocarbons and hydrocarbon classes. Use of vacuum ultraviolet (130 to 300 nm) circular dichroism (CD) is under investigation as a means of monitoring optically active hydrocarbons eluting from a gas chromatograph (GC). This GC/CD system is using the National Synchrotron Light Source U9A Beamline. The spectral and thermal properties of ozone-chemiluminescence as a means of monitoring hydrocarbon classes (e.g., reduced sulfur compounds, olefins, and so forth) and photothermal laser spectroscopies are also being investigated as selective and sensitive devices for chromatographic detection. [1.8 FTE]

126. Analytical Techniques with Synchrotron Radiation and Ion Beams

K.W. Jones, B.M. Gordon

This project develops new analytical methods for elemental determinations and chemical speciation using synchrotron radiation from the National Synchrotron Light Source. Equipment is being developed to produce a focused monoenergetic x-ray beam with a spatial resolution in the neighborhood of 10 micrometers. Other apparatus has been assembled that uses a collimator with either monoenergetic x-rays or white radiation to produce beams with sizes around 30 micrometers. The x-rays from the NSLS will have energies between about 4 and 20 keV, which will make possible investigation of all elements in the periodic table with $Z > 10$. Techniques for precise trace element measurements with minimum detectable limits approaching one part in 10^9 are being developed concurrently for both bulk and microanalysis. Chemical speciation will be achieved by use of precision x-ray energy measurements and electron spectroscopy techniques. A searching test of the new methods is made by comparison of the results obtained with synchrotron radiation with those obtained by other methods. These tests require the application of the techniques to samples obtained from a variety of energy-related fields. The use of synchrotron radiation for elemental quantification is supported by the use of nuclear ion-beam analysis, which makes available complementary analytical techniques that are used to corroborate and extend the synchrotron radiation results. [4.4 FTE]

Chemistry Department $90,000

127. Applications of Nuclear Methods to Analysis

G. Harbottle, E.V. Sayre, R.W. Stoenner

This project is concerned with the extension and improvement of nuclear methods of elemental analysis, particularly methods that permit the determination of many components (including trace impurities) quickly and efficiently, and with the development of computer-based multivariate statistical analysis, which will permit the efficient and effective analysis of large assemblages of such analytical data. These methods are being applied to a wide variety of materials for which geographic origins are of significant interest. The effects of geochemical processes on trace element patterns are being investigated in several natural materials and artifacts made from them. Studies of the accuracy and precision of standardization in activation analysis are an important part of the project. [1.2 FTE]

Idaho National Engineering Laboratory
Idaho Falls, Idaho 83401

EG and G Idaho, Inc. **$126,000**

128. *Negative Ionization Mass Spectrometry*
J.E. Delmore

This project studies two ionization processes for application to negative ion mass spectrometry: negative surface ionization and electron capture. Surface ionization studies are focused on systems where the species of interest is chemisorbed on a low work function surface, followed by thermal desorption. To date, ions studied by this method include Cl^-, Br^-, I^-, BO_2^-, CN^-, CNO^-, and H^-. Ionization efficiency has been increased by several orders of magnitude using this technique. A unique electron capture ion source using crossed electric/magnetic fields has been theoretically modeled, designed, constructed, and tested. This ion source forces electrons into a cycloidal orbit to reduce the kinetic energy to thermal values. The thermalized electrons are readily captured by gas molecules to form negative ions, without the high pressure system otherwise required for electron capture mass spectrometry. Refinement of both the experimental model and instrumentation is the next major thrust of the project. [1.0 FTE]

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Physics Division **$167,000**

129. *The Formation and Properties of Complexes of Helium and Hydrogen Isotopes*
R.D. Taylor

The conditions for formation and the properties of a metastable, bound-state complex of ^3He and tritium are under study. T_2 decays with a half life of 12.3 years, ultimately producing a pair of ^3He atoms. However, vapor pressure-time measurements show that the ^3He formed in liquid T_2 is retained in the liquid in an amount far exceeding the ordinary solubility. This complex, once formed, is found to be unstable in the gas phase, but it is virtually stable in liquid or in solid tritium. Data for solid T_2 at 20.0 K suggest that the newly formed ^3He is also bound. The electrical conductivity of solid T_2 containing the complex shows an initial decline of about a factor of five from the conductivity of the liquid. After a few days, this conductivity is about 100 times less. A new cell allows pressure buildup measurements of liquid or solid T_2 without the complication of gas phase corrections. Other time-temperature measurements to characterize the complex include magnetic susceptibility and compositional studies of successive portions of gas removed from the cold cell. [1.3 FTE]

Monsanto Research Corporation-Mound
Miamisburg, Ohio 45342

Nuclear Operations Department **$710,000**

130. *Isotope Separation Research and Development*
W.M. Rutherford, B.E. Jepson, E.D. Michaels, W.R. Wilkes

This project will investigate chemical exchange and liquid phase thermal diffusion as techniques for stable isotope separation. The chemical exchange work is directed toward finding significant equilibrium isotope effects in metal isotope exchange reactions emphasizing macrocyclic complexants to develop two-phase isotope exchange processes for practical separations. The liquid thermal diffusion work is directed toward (1) further development of the recently discovered relationship between the elementary liquid phase thermal diffusion effect and molecular mass and structure and (2) acquiring an improved understanding of the behavior of the liquid phase thermal diffusion column and its application to the separation of stable isotopes. [3.6 FTE]

131. *Atomic and Molecular Properties and Their Relationships to Separation Processes*
W.L. Taylor, G.T. McConville

The objective of this research is to investigate physical properties of isotopes and their mixtures pertinent to the development or improvement of new or existing technologies. Experimental and theoretical work on gas transport properties and thermodynamic properties of gases, liquids, and solids is being conducted and applied to improving methods of isotope separation and the use of isotopes and their mixtures. Thermal and ordinary diffusion coefficients are being measured and separation processes studied in the context of non-equilibrium thermodynamics. This project also investigates several properties of the hydrogen isotopes and their spin isomers. Experiments are being carried out to determine the isotopic exchange rate between deuterium and tritium at low temperatures and to characterize the effect of trace impurities and surface conditions on the exchange rate. A system is being prepared to separate the nuclear spin isomers of deuterium. Specially constructed cells loaded with ultra high purity deuterium produced at Mound are being evaluated as part of an international effort to get the triple point of D_2 established as a fixed point in the International Temperature Scale. Theoretical studies on the hydrogen molecule interaction have produced the best available spherically symmetric intermolecular potential for the hydrogen isotopes. Current work is aimed at incorporating the angle dependence into the collision dynamics. [3.3 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Analytical Chemistry Division $1,410,000

132. R&D in Secondary Ion Mass Spectrometry
W.H. Christie, R.E. Eby, P.J. Todd

Rapid growth has occurred in recent years in particle sputtering as a means for producing atoms and ions for mass spectral analysis. More recently it has been observed that secondary ion mass spectometry (SIMS) offers a means of studying organic and inorganic materials. The focus of our research has shifted in this direction, and our approach to organic SIMS has been to interface an in-house developed secondary ion source with a tandem three-sector mass spectrometer. This combination is being used to investigate the chemistry and physics of secondary ion emission from both volatile and involatile organic species. In inorganic SIMS, we are investigating laser induced resonance ionization of sputtered neutrals using a recently acquired microbeam instrument that has been modified for these studies. Fundamental information concerning the sputtering process is being obtained since resonance ionization allows one to probe the excited electronic states of neutral atoms ejected during a sputtering event. Experiments have been performed with samarium and uranium, which demonstrate the number and type of ions formed along with optical spectral information showing the wavelengths at which resonance ionization occurs. [2.0 FTE]

133. Mass Spectrometry R&D for Organic Analyses
G.L. Glish, P.J. Todd, E.H. McBay, S.A. McLuckey

This project consists of studies in two general areas of organic mass spectrometry: (1) mass spectrometry/mass spectrometry (MS/MS) and (2) ionization/excitation processes. Both are experiencing rapid growth in popularity as analytical techniques even though much is yet to be understood about the underlying chemical and physical principles. The main thrust is to investigate the chemical and physical phenomena associated with these areas to increase understanding and therefore make application easier for the general mass spectrometrist. The studies of these areas are in many ways complementary. MS/MS is a very good tool to study gas phase ionic structures and thus can be used to help elucidate chemical processes that occur during ionization. Conversely, various ionization methods can be used to generate unique types of ions which can be used to assist in extending the understanding of MS/MS. Of particular interest is the gas phase ion chemistry and physics involved in MS/MS. Studies in these areas will not only elucidate the basic phenomena in MS/MS, but also the basic processes in mass spectrometry in general. [2.2 FTE]

134. Advanced Spectroscopic Methods for Chemical Analysis
L.D. Hulett, J.M. Dale, T.M. Rosseel

This project applies electron, positron, x-ray and heavy ion physics, and mass spectroscopy to analytical problems. Positron spectroscopy is being evaluated for characterization of surfaces and bulk materials, chemical analyses, surface area measurements, and solid state defect studies. Monoenergetic positron sources (developed earlier in this project) and the ordinary fast sources are being used. Ions from the EN Tandem Accelerator and the Holifield Heavy Ion Facility are being used to induce heavy ion x-ray satellite emission spectra (HIXSE) for studies of valence states of metal alloys and other materials. Scanning and transmission electron microscopy are used in conjunction with and in support of all of these activities. The positron and heavy ion methods are being developed for use in other programs. Other groups at State University of New York-Fredonia, Duke University, and University of Missouri are collaborating with this project. [2.8 FTE]

135. Research Development and Demonstration of Advanced Chemical Measurement Techniques
H.H. Ross, J.M. Ramsey, R.W. Shaw, W.B. Whitten, J.P. Young

New spectroscopic and instrumentation techniques are being developed that have the potential of meeting critical measurement needs in the analytical community. A new project that employs lasers and phase conjugate optics has led to a whole new concept in laser scanning systems. Time resolved fluorescence spectroscopy is being developed for a broad range of important analytical applications. Fourier transform microwave spectroscopy is being pushed for the rapid quantification of complex organic and inorganic mixtures. A new computer system is being programmed to collect data for this project as well as to carry out the fast Fourier transform processing that is needed. Several new laser systems are being investigated for application to diagnostic studies of plasmas used in chemical vapor deposition experiments. We are starting a new research program that exploits robotics in analytical chemistry. [3.8 FTE]

136. Mass Spectrometric R&D for Inorganic Analyses
R.L. Walker, H.S. McKown, D.H. Smith, D.L. Donohue

The objective of this research is to improve isotopic ratio mass spectrometry and to extend its areas of application. Areas of improvement are being sought in instrumentation and methodology, precision of analysis, and elemental specificity. Our laboratory houses state-of-the-art, high sensitivity, multi-staged mass spectrometers to provide high quality isotopic ratio measurements on extremely small samples (~1 ng). Low-level separations techniques are carried out in a Class 100 clean room, and isotope dilution is used extensively for quantification. Resonance ionization mass spectromery is an area of continuing, strong research. Basic studies to elucidate the resonance ionization process will be conducted. In this effort, a laser has been interfaced to a time-of-flight mass spectrometer to study the temporal variation of evaporated species. Development of a workable hollow cathode ionization source will be evaluated. The goal is to devise a better means of ionizing elements with high volatility and high ionization potential (e.g., mercury, technetium, osmium). [2.5 FTE]

Chemical Technology Division $1,410,000

137. Chemical and Physical Principles in Multiphase Separations
C.H. Byers, R.M. Wham, C.D. Scott, J.S. Watson, T.C. Scott

Fundamental chemical engineering investigations include new concepts and basic understanding of multiphase separation methods. Fluidized and expanded beds are stabilized by the imposition of an electric field, thus exhibiting the desirable sorption characteristics of fixed beds, while the pressure drop is approximately half the fixed bed. The applicability of this principle to a novel method for slurry bed sorption is under study. Mass transfer enhancement in dispersed-phase systems by forcing the oscillation of small droplets in a continuous medium is being investigated. Preliminary results show that droplet motion can be forced by an oscillating electric field. A study to investigate separation phenomena associated with the formation of droplets in liquid-liquid systems under the influence of electric fields has been initiated. Stability theory and mass transport behavior are under investigation. [5.3 FTE]

138. Solvent-Solute Interactions in Separations with Supercritical Solvents

H.D. Cochran, C.D. Scott

Theoretical and experimental studies focus on the molecular interactions between solvent and solute in supercritical solutions, which are important in understanding supercritical separations methods. Theoretical analysis aims to relate solubility to a potential function for the solvent-solute interactions using a theoretically-sound equation of state. A new expression for the fugacity coefficient in a mixture of hard, convex bodies represents the repulsive interactions between molecules of disparate size and shape. Virial terms from the hard core Kihara potential represent the attractive effects between nonpolar molecules. Future work will involve representing the effects of molecular polarity. Initial experiments focus on solubility of moderately volatile inorganic fluorides (WF_6, MoF_6, UF_6, RhF_6, IrF_6) in supercritical CF_4. Subsequent studies with $CClF_3$ and CH_3F will explore effects of solvent polarity in support of the analysis. Using inorganic solutes and halomethanes will broaden the data base for supercritical solubility and may lead to separations of importance to DOE's nuclear programs. After solubility studies become routine practice, ^{19}F-NMR spectroscopy studies of the supercritical solutions are planned to provide independent and complementary measures of the solvent-solute interactions. [1.7 FTE]

139. Sorption in Separations

P.W. Fisher

Many chemical separations involve sorption as either the primary separation phenomenon or as an important step in the separation mechanism. Whenever a mixture is brought into contact with a surface or substrate to affect a separation, the first step at the surface is always adsorption and the last step is always desorption, regardless of the intervening steps. Emphasis in this project is placed on developing a fundamental understanding of the dynamics of sorption. Much related work done in the past has been concerned with highly active surfaces important to heterogeneous catalysis. But this project is directed toward low activity surfaces encountered in separations. The focus on less active surfaces allows meaningful theoretical evaluations to be made while focusing on an important area of science currently receiving little attention. In this work macroscopic effects are related to microscopic properties of the gas, solid, and adsorbed phases using selected theoretical models. This approach improves our scientific understanding of separations, while maintaining applicability of the work to a broad spectrum of problems in which sorption is important. [1.4 FTE]

140. Chemistry of Actinides and Fission Products

L.M. Toth, D.J. Pruett, S.A. Sherrow

This project aims to develop the fundamental chemistry of the actinide elements and their fission products. Specific areas of focus include: (1) photochemical studies of the aqueous actinides (uranium, neptunium, and plutonium); (2) the characterization of structures and properties of actinide and mixed actinide polymer materials; (3) the photochemistry of low temperature uranium and plutonium frozen solutions or salts, with particular interest on isotope effects and differences; (4) kinetic and thermodynamic studies of complexation and redox reactions in aqueous and nonaqueous systems; (5) determination of solvation numbers in aqueous and nonaqueous systems; (6) properties of complexes with macrocyclic ligands; (7) dissolution mechanisms of refractory metal oxides; (8) aqueous zirconium chemistry and redox ruthenium chemistry to establish chemical properties that determine separation and control of these fission products in fuel reprocessing; and (9) studies of the fundamental properties of aqueous and nonaqueous solvent systems in support of these primary fields of investigation. Future plans include studies of catalytic effects of plutonium(IV) and uranium(IV) on actinide redox reactions, particularly the neptunium(VI → V → IV) reaction. [3.0 FTE]

Chemistry Division $1,250,000

141. Chemical and Structural Principles in Solvent Extraction

C.F. Baes, Jr., J.H. Burns, W.J. McDowell, B.A. Moyer

This research focuses on the fundamental role of molecular bonding and structure in determining the chemical selectivity and physical behavior of solvent extraction systems. The findings should also apply to other phase-transfer separation systems employing membranes or ion-exchange resins. The experimental approaches include: (1) measurements that determine systematically the effect of extractant type and structure on the extraction of a variety of metal ions, (2) more detailed equilibrium and other measurements of selected systems to describe more fully the reactions involved, (3) diffraction and spectrometric studies of structures in solids and solutions, and (4) design and synthesis of new and improved extractants. Extensive systematic studies and, for selected systems, more detailed measurements of extraction behavior are currently being conducted on acidic, neutral, and basic extractants and on synergistic combinations of macrocyclic and acidic extractants. Reagent combinations found to have potential practical value as extractants or that are interesting theoretically are being studied further by x-ray diffractometry of solids and liquids, and by NMR and infrared spectrometry of the liquids. Increased emphasis is being placed on the design and synthesis of new macrocyclic compounds that may have promise as separation agents. Finally, detailed measurements are being made of the role of hydrolysis in the extraction of metal ions. [5.0 FTE]

Pacific Northwest Laboratory
Richland, Washington 99352

Biology and Chemistry Department $180,000

142. *Fundamental Phase Partitioning in Supercritical Fluid Chromatography*
R.D. Smith, C.R. Yonker

The goal of this project is a fundamental understanding of the kinetic and thermodynamic constraints upon partitioning of a solute between a supercritical fluid and a supported phase. The project involves investigation of fluid phase reactivities, solubilities, and phase partitioning kinetics relevant to supercritical fluid chromatography and extraction phenomena. Phase partitioning and related chromatographic processes are being studied using direct fluid injection-mass spectrometry, classical equilibrium sampling, and solvatochromic techniques. Focus is on gaining an understanding of chromatographic processes for polar amd mixed supercritical fluid and solute systems and the kinetic and thermodynamic limitations upon separations in supercritical media. Experimental results are being compared with both theoretical methods for prediction of fluid phase solubilities and actual chromatographic separations for model systems, with the aim of identifying critical parameters for developing improved chromatographic systems. [1.0 FTE]

Radiological Science Department $725,000

143. *Analytical Mass Spectrometry Research*
R.L. Gordon, J.M. Kelley, D.M. Robertson, J.J. Stoffels, R.A. Warner

This project develops new knowledge and techniques to extend the application of mass spectrometry to problems in chemical and isotopic analyses. The project: (1) elucidates physicochemical mechanisms responsible for efficient ion production in isotopic analysis by surface ionization mass spectrometry; (2) develops methods for the control of surface work function of ion sources; (3) develops techniques for application of mass spectrometry to real-time analysis; and (4) establishes new ionization techniques. Surface analytical tools are used to establish physical and chemical properties of surface ionization sources and to identify chemical pathways responsible for ion production. The direct-inlet technique for real-time mass spectrometry uses innovations in ion sources, mass separators, and ion detectors. Laser-assisted ionization is being developed for new mass spectrometry ion sources. [3.3 FTE]

144. *Analytical Atomic Absorption Spectrometry Research*
D.L. Styris, J.H. Kaye

This project elucidates experimentally the mechanisms that control sample vaporization in furnace atomic absorption (FAA) spectrometry. Vaporization models developed from these results provide understanding of chemical treatment and furnace effects, and thus establish the basis needed to help broaden and improve application of contemporary FAA spectrometric analysis. The neutral atoms, ions, and molecular species that appear in vapor phases during the temperature rise of the furnace are monitored simultaneously by atomic absorption and mass spectrometric techniques. Correlation of results from these experiments with furnace temperature and applications of chemical thermodynamic and kinetic data help to identify and characterize the controlling chemical and physical processes. Vitreous carbon, tantalum, and graphite furnace materials are being used presently in order to model the Group IIA element vaporization that occurs in presence of these furnace materials and the intragroup matrix modifiers. The experimental technique is also being used to verify theoretical models of vaporization (e.g., vaporization of selenium and the influence of nickel as a stabilizer). [1.2 FTE]

145. *Laser-Based Analytical Techniques*
T.J. Whitaker, B.A. Bushaw, B.D. Cannon

The project objective is to develop and evaluate ultra sensitive and highly selective laser-based analytical techniques for detection and measurement of trace substances produced as a result of energy research and production using photon correlation techniques to provide sensitive, selective analyses. These techniques rely upon multiple resonant scattering by a single atom as it passes through a laser beam to measure the difference between the rate of photomultiplier counts when there is an analyte atom in the laser beam and when there is not. These methods are very effective at discriminating against background counts and in suppressing Lorentzian tails of normally interfering species so that spectral interferences are greatly reduced. We are developing photon correlation techniques for several elements that normally exist in solid form. Quantitative methods are being developed to atomize these samples so that the extreme sensitivity of the measurements can be correlated to actual concentrations in real samples. An important aspect of this work is the development of photon correlation analysis for atoms in metastable electronic states. This work will extend the applicability of photon correlation methods to many more elements than currently possible, including noble gases. [1.2 FTE]

Chemical Engineering Sciences

Lawrence Berkeley Laboratory
Berkeley, California 94720

Applied Science Division $261,000

146. *Turbulent Combustion*
F. Robben, R.K. Cheng, L. Talbot

The interaction between fluid dynamic turbulence and chemical reaction in premixed turbulent combustion flows is being studied experimentally using laser diagnostic techniques. The objective is to elucidate the turbulent combustion processes and to provide data for comparison with theoretical models. The experimental flow configurations used in this study are idealizations of those found in practical premixed combustors. They are (1) heated wall turbulent boundary layer capable of supporting combustion in fuel lean mixtures, (2) rod-stabilized turbulent v-flame, and (3) Bunsen-type conical turbulent flame. A two-point Rayleigh scattering technique measures the density fluctuations simultaneously at two points and yields the temporal and spatial scales of the flame structure. This technique is being extended to 512 points through use of a linear array camera and image analysis system. Conditional velocity fluctuations and covariance are determined using a two-component LDA system and are being applied to the study of velocity statistics in the

Bunsen flame, for comparison with the v-flame results. A deterministic theoretical simulation of the v-flame, based on the random vortex technique, is being developed. The results, which will be compared with the experimental data, will further the understanding of the turbulent flame-flow interaction process. [2.5 FTE]

Materials and Molecular Research Division **$150,000**

147. *High-Pressure Phase Equilibria in Hydrocarbon-Water (Brine) Systems*
J.M. Prausnitz

Phase equilibria are required for efficient design of large-scale separation processes (e.g., distillation and extraction) in the chemical and related industries. In this context, efficient refers to optimum use of raw materials and to conservation of energy. Since the variety of technologically-important fluid mixtures is extremely large, it is not possible to obtain all desired equilibria from experiment. Therefore, the objective of this research is development of molecular thermodynamics for interpretation and correlation of selected phase-equilibrium data toward reliable general prediction of phase equilibria for engineering. The correlations are expressed through semi-theoretical physicochemical models in a form suitable for computer-aided design. In this research, particular attention is given to those systems that are of primary interest in energy-related industries, especially those concerned with fossil fuels and fossil-fuel-water mixtures. Development of molecular thermodynamics calls for a combination of theoretical, computational, and experimental work. Further, it demands simultaneous awareness of progress in molecular science and of realistic requirements for engineering design. [2.2 FTE]

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Theoretical Division **$80,000**

148. *Thermophysical Properties of Mixtures*
J.J. Erpenbeck

The thermophysical properties of mixtures of particles interacting through the hard-sphere potential are evaluated, using both the equilibrium techniques of Monte Carlo (MC) and molecular dynamics (MD), as well as non-equilibrium molecular dynamics (NEMD). The properties under investigation include both the equation-of-state and transport properties. The latter include mutual diffusion, shear and bulk viscosity, and thermal conduction. A combined MC-MD calculation for the single-component hard-sphere fluid has yielded equation-of-state data of sufficiently high precision to enable us to estimate the sixth and seventh virial coefficients and to obtain Pade's approximants for the pressure that fits the MC-MD data over the fluid regime, up to a density of 1/1.6 of close-packed. The study of the shear viscosity of the hard-sphere fluid by NEMD has shown the existence of a shear-induced phase transition to a two-dimensionally ordered phase. This same study shows the viscosity coefficient to decrease regularly with increasing shear rate up to the phase transition. For the case of isotopic (mutual) diffusion, comparisons of Green-Kubo and NEMD calculations have shown the methods to agree, yielding a mutual diffusion constant roughly 15% greater than the prediction of the Enskog theory, for a volume three-times close-packing. The enhanced diffusion appears to arise from the existence of a long-time (perhaps $t^{-3/2}$) tail in the velocity-velocity time correlation function. The velocity autocorrelation function for hard spheres has been evaluated for a wide range of fluid densities and compared with predictions of mode-coupling theory. The results strongly support the existence of long-time tails in three dimensions. [0.5 FTE]

National Institute for Petroleum and Energy Research (NIPER)
Bartlesville, Oklahoma 74005

Processing and Thermodynamics Division **$177,000**

149. *Thermodynamic Characterization of Condensed-Ring Compounds*
B.E. Gammon

Research continues on the thermodynamic characterization of condensed-ring organic hydrocarbons, as well as on organic oxygen, nitrogen, and sulfur compounds. Results are used from an experimental program that provides enthalpies of combustion, condensed-phase heat capacities for fluid-phase property behavior from very low temperatures and for third-law entropy determinations, vapor pressures, enthalpies of vaporization, vapor-heat capacities, and molecular statistical thermodynamic properties for the ideal gases from Raman and infrared spectroscopy. The results are used to settle fundamental questions and to provide extensions to methods of prediction of thermodynamic properties from *ab initio* molecular orbital calculations and from semiempirical correlations based on molecular structure. Properties of concern include chemical thermodynamic properties (Gibbs energies, entropies, and enthalpies of formation) as well as thermophysical properties. The influence of heteroatoms, strain, and non-bonded intramolecular interactions are investigated, as is the influence of strong intermolecular interactions (e.g., hydrogen bonding, dipole interactions, molecular shape, internal bond strengths, and other conventionally recognized intermolecular forces). [3.0 FTE]

Sandia National Laboratories
Livermore, California 94550

Thermofluids Division-8363 **$240,000**

150. *Analysis of Reacting, Turbulent Flows*
W. Ashurst, P. Barr, B. Sanders

This research focuses on understanding the detailed mechanisms of heat, mass, and momentum transfer in the mixing region of reacting shear flows. Activity involves development of an unsteady turbulence computational procedure for application to flows with high Reynolds numbers and large heat release. The vortex dynamics simulation procedure will be used to study the transport of a conserved scalar in both homogeneous and inhomogeneous turbulent flows in two- and three-space dimensions. This procedure is unique in that it relaxes some of the restrictive assumptions employed in most conventional turbulence models, and the method is capable of resolving the time-dependent coherent structures that have a first order influence on the transport of chemical species. A hybrid computational scheme will be constructed using the Lagrangian vortex dynamics procedure for small-scale turbulent structures, and the Eulerian large-eddy simulation procedure for large-scale structures. This hybrid method shows promise for a major breakthrough in turbulence modeling, as the time-dependent flowfield can be described over a wide range of length scales important to combustion. [1.5 FTE]

Heavy Element Chemistry

Argonne National Laboratory
Argonne, Illinois 60439

Chemistry Division **$1,330,000**

151. Heavy Element Chemistry Research
W.T. Carnall, J.V. Beitz, L. Soderholm,
L.R. Morss, J.C. Sullivan

The heavy elements project is a long-range research effort to advance our understanding of the chemistry and physics of the actinide elements. Bonding and reactivity of actinides in key compounds and in solutions are probed by the systematic comparison of their properties (1) among several members of the 4f and 5f series, (2) in parallel oxidation states, or (3) in the same coordination sites. Emphasis is placed on the development of models that will aid in predicting the properties of unexplored systems. Novel inorganic and organometallic compounds are being synthesized to extend the limits of known stability relationships. The dynamic and thermodynamic parameters that characterize oxidation-reduction reactions of actinides in aqueous solutions are probed using state-of-the-art pulse radiolysis and stopped-flow methods. Such efforts stress the importance of modeling as a method of gaining an understanding of the behavior of actinides in process chemistry and in the aquatic environment. Efforts in spectroscopy, photophysics, and photochemistry are increasingly addressing higher valent reactive compounds of neptunium, plutonium, and americium, and are related to DOE programmatic interests in isotope separation. New opportunities are being exploited to broaden our understanding of electronic structure by focusing on the unique properties of curium, berkelium, and californium compounds. [10.1 FTE]

Lawrence Berkeley Laboratory
Berkeley, California 94720

Materials and Molecular Research Division **$1,250,000**

152. Actinide Chemistry
N.M. Edelstein

The project objective is to study actinide materials to provide the basic knowledge necessary for their safe and economic use in present and future technology. The project includes preparation of new gaseous, liquid, and solid phases and studies of their physical and chemical properties. Techniques for characterization include x-ray diffraction, optical and vibrational spectroscopy, magnetic resonance, and magnetic susceptibility. Equilibrium and kinetic data for complex formation are measured. From these complementary studies, new insights into the structural and chemical principles of actinide compounds are obtained to design new synthetic schemes to produce new materials. A major aspect is the design and synthesis of sequestering agents for actinide ions. These compounds are intended for use in the treatment of actinide poisoning and for possible application in the treatment of spent reactor fuels. Preparative, structural, and physical studies of new types of organoactinide, related organolanthanide, and new actinide inorganic complexes are continuing. Studies on optical spectra of free ions and actinide ions in crystals are being pursued in order to understand their electronic structure. [15.0 FTE]

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Isotope and Nuclear Chemistry Division **$270,000**

153. Actinide Valence, Host, and Radiation Effects
P.G. Eller

There is only sparse information regarding valence stabilities of the transuranium elements plutonium, americium, and curium in solids important to nuclear waste storage. We are determining the effects of ion size and radiation on actinide valence stabilities and site selectivities, particularly of americium(III, IV) in selected oxide matrices. Since plutonium, americium, and curium have profoundly different aqueous valence stabilities, we anticipate stability differences when they are incorporated in solids and exposed to radiation (self-radiation or other). We have developed an approach to predicting actinide valence stabilities and site selectivities in solids and are determining the validity of the hypothesis by synthesizing and studying appropriate actinide materials by spectroscopic and diffraction techniques. We also continue appropriate solid state and solution characterization of oxo and fluoride species (e.g., MO_2^+, MOF_4, and so forth). In addition to the obvious relevance to practical nuclear waste storage considerations, the work will also contribute to the general physicochemical understanding of actinide behavior in condensed phase systems where oxygen is the coordinating ligand, either as free oxide ion, or when connected to another element (e.g., silicon, phosphorus, and so forth). [0.9 FTE]

154. Actinide Chemistry in Near-Neutral Solutions
D.E. Hobart, T.W. Newton

We are investigating a spectrophotometric method for determining the carbonate complexes of plutonium(IV) and their association quotients. The method involves competition between citrate and carbonate ligands for the plutonium. Values for the formation quotients for the citrate complexes are available in the literature, but will be checked for applicability under our experimental conditions. The experiments are done on solutions saturated with argon containing known partial pressures of CO_2 in order to fix the thermodynamic activities of CO_2 and H_2CO_3. Preliminary experiments have shown that significant spectral changes occur when the pH is changed at constant citrate concentrations and when the citrate/bicarbonate ratio is changed at essentially constant pH. Measurements on solutions where each contains no citrate, but has a different pH and constant CO_2 pressure indicate the presence of at least three carbonate-containing complexes in the pH range from 7 to 9.5. One or more of these may be hydroxo- or bicarbonato-complexes. Spectral data are taken at 10 wavelengths between 400 and 700 nm. A non-linear least-squares program is being adapted for the quantitative interpretation of the data. [0.9 FTE]

Materials Science and Technology Division $115,000

155. Thermodynamics of the Transplutonium Elements and Early Actinides

P.D. Kleinschmidt, J.W. Ward

Fundamental thermodynamic data are obtained on actinide elements, compounds, and alloys by using high temperature mass spectrometry and target collection techniques. The sublimation pressures of the pure metal, protactinium, are being measured. The cohesive energy is derived from these numbers and is correlated with the electronic structure of the element. From vapor composition measurements on the americium and protactinium oxides and plutonium and neptunium fluorides, the entropy and enthalpy of sublimation are determined as well as the bond dissociation energies of the gas phase molecules. The actinide series is the only one in which f electrons participate in bonding; the effect of this is to produce unique structures and compounds. These numbers will provide a data base for any study involving transplutonium elements and compounds. Fast breeder reactor technology will require such information, as will waste storage and disposal studies. [0.8 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Chemistry Division $1,250,000

156. Chemistry of Transuranium Elements and Compounds

O.L. Keller, J.K. Gibson, R.L. Hahn, R.G. Haire, G.D. O'Kelley

The project emphasizes the role of 5f electrons and of relativistic effects in determining the chemical and physical behavior of the actinides. Fundamental studies include: (1) investigation of the changes in 5f bonding characteristics in actinide metals and compounds as a function of pressure (up to 57 GPa); (2) derivation of thermodynamic properties of metals and compounds from high temperature Knudsen cell/mass spectrometer measurements; and (3) determination of hydration and complexation phenomena by neutron and (synchrotron) x-ray diffraction. A new direction is being developed as a result of recent renewed interest in proposed studies of the chemistry of element lawrencium, the last of the 5f electron series, and of the transactinide elements, in which the 7s, 7p, and 6d electrons are important. These elements could be produced in relatively large yields at accelerators using a 40μg ^{254}Es target, if the necessary financial support is obtained. Currently, the chemical identification of lawrencium and the determination of the radius of the 3^+ ion is being carried out on the basis of 20 atoms per bombardment using a 3μg ^{254}Es target. Measurements are planned of the chemical reduction of Lr^{+3} to metal in order to estimate the value of the $Lr^{+3}Lr^0$ couple. Searches will be made for lower oxidation states (especially Lr^{+1}) to study possible relativistic stabilization of the $7s^2$ orbitals vs. the 7p or 6d. [9.0 FTE]

OFFSITE INSTITUTIONS

Photochemical and Radiation Sciences

University of Alabama
Tuscaloosa, Alabama 35486

157. ELDOR Investigations of Radiation Processes
L.D. Kispert **$71,200**
Department of Chemistry

The objective of this research is to determine how a lattice affects energy transfer and primary radiation and photochemical processes in irradiated organic crystals and glasses. Such information is vital to understanding photosynthesis, photoinduced solid-state polymerization, electron and hole transport, and stereospecific reactions in solids. Electron spin resonance, electron-nuclear double resonance, and electron-electron double resonance techniques are being used to identify the molecular fragments formed and to detect the energy transfer processes that occur. In particular, selected polyene, paraphenylene oligomers, sugar, carboxylic acid, and acetamide crystals are being studied to determine the effect of host lattice on radical stability and reaction mechanisms as a function of temperature in crystals containing (1) varying crystallographic forms, (2) rotational disorder, and (3) impurities. Preexisting electron traps, first observed by this research, have been studied in crystals of rhamnose and trehalose, radical intermediates have been identified in irradiated beta-carotene, the effect of carotenoids on the photoexcited triplet state lifetimes of porphines and the excited singlet lifetimes of carotenoids have been measured, and organic anions and cations have been detected and characterized.

Alabama A and M University
Normal, Alabama 35762

158. Photoacoustic-Laser Spectroscopy of Halogens and Mixed Halogens for Energy Purposes
P. Venkateswarlu **$100,000**
Department of Physics **(24 mo.)**

A photoacoustic spectrometer for a study of the energy level structure of halogen and mixed halogen molecules is being assembled. A nitrogen laser-pumped dye laser system is used as the excitation source. Acoustic signals are detected with an electret microphone fixed in a quartz absorption cell containing the halogen molecules along with a buffer gas. Signal processing is performed by a box car integrator. Wavelength calibration is achieved by a simultaneous recording of the optogalvanic spectrum of neon or argon along with the photoacoustic signal on a Hewlett-Packard plotter. A recent recording of these optogalvanic signals in neon and argon using hollow cathode lamps have given spectra with good signal to noise ratio. It is planned to record both low resolution and high resolution photoacoustic spectra. The low resolution spectrum gives us the vertical points in the upper electronic states from where non radiative relaxations/decays take place. The high resolution spectrum gives information regarding the perturbations and non-radiative relaxations among the vibrational-rotational levels of the excited electronic states.

University of Arizona
Tucson, Arizona 85721

159. Mechanisms of Photochemical Energy Conversion by Chlorophyll
G. Tollin **$86,300**
Department of Biochemistry

The goals of this project are (1) to elucidate the detailed mechanisms involved in light-induced one-electron transfer reactions involving chlorophyll (and related compounds), electron donors, and acceptors; and (2) to determine the interactions between the elementary steps in these processes and environmental parameters such as viscosity, dielectric constant, and homogeneous vs. heterogeneous reaction matrices. The intent is to develop a body of fundamental information that can be used to devise strategies for increasing the yields of the high energy products of such reactions, to physically separate these products and to decrease the probability of recombination (i.e., back reaction), and to facilitate secondary electron transfer to external donors and acceptors. Current work involves the use of laser flash photolysis to monitor excited state and radical dynamics in lipid bilayer vesicle systems.

Battelle-C.F. Kettering Research Laboratory
Yellow Springs, Ohio 45387

160. Particulate Models of Photosynthesis
G.R. Seely **$70,000**

The project consists of the investigation of photophysical and photochemical properties of chlorophyll, adsorbed together with other amphiphilic molecules on particles of polyethylene swollen with low molecular weight diluents. The swollen particles provide a viscous base for anchoring the hydrocarbon moieties of the amphiphiles, which helps protect chlorophyll excited states from dynamic quenching processes. The states of chlorophylls on these particles are especially characterized by their fluorescence spectra, quantum yields, and lifetimes, which depend on the amphiphiles adsorbed with chlorophyll. The present focus of our efforts is on the photochemistry of these particles suspended in an aqueous medium when various oxidants and reductants are added, especially those in which separation of products into different phases occurs, and on determining the nature of the excited states responsible for the reactions.

Boston University
Boston, Massachusetts 02215

161. Investigation of the Triplet States of Chlorophylls
R.H. Clarke **$89,993**
Department of Chemistry

The characterization of the structures assumed by chlorophyll molecules upon aggregation in photosynthetic systems is important for an understanding of the mechanisms of energy conversion in photosynthesis. Since the properties of the excited triplet state of the pigment molecules such as the electron distribution and excited state dynamics are sensitive to the surrounding interactions and to the state of aggregation, triplet state properties serve as a convenient and nondestructive probe into the makeup of photosynthetic systems. Our present research project uses optical detection of magnetic resonance spectroscopy, raman spectroscopy, and raman-detected magnetic resonance to investigate the triplet state properties of the chlorophyll molecule in lipid bilayers, in protein matrices, and as films deposited on surfaces. These measurements allow an evaluation of *in vitro* chlorophyll systems for structural features proposed as models for the antenna and reaction center of naturally occurring photosynthetic systems and for their general applicability as model systems for photosynthesis.

162. Study of Intermediates from Transition Metal Excited-State Electron-Transfer Reactions

M.Z. Hoffman **$80,000**
Department of Chemistry

Excited-state inter- and intramolecular electron-transfer reactions lie at the heart of most photochemical solar energy conversion schemes. Using the techniques of continuous and pulsed photolysis and radiolysis, this project examines the kinetic and mechanistic behavior of intermediates that result from excited-state electron-transfer reactions involving transition metal coordination complexes, electron donor–acceptor complexes, quenchers, and sacrificial electron donors in solution. The work has focused on three general aspects of these reactions: (1) the effect of solution medium on the properties and quenching of the excited states, (2) the control of the quantum yield of formation of redox products, and (3) the mechanisms by which reduced species interact with water to yield H_2 homogeneously and heterogeneously. To better understand the fundamental chemistry governing the generation of energy-rich charge-separated species, we have examined specifically (1) the reactions of viologens with radiation-generated EDTA-radicals; (2) the yield of reduced viologens in photochemical systems containing ruthenium(II)-polypyridyl complexes, viologens, and sacrificial electron donor-acceptor complexes between viologens and anionic electron donors; (4) the thermal reduction of methyl viologen in alkaline solution; (5) the interaction of reduced viologens with redox catalysts; and (6) the photophysics of chromium(III)-polypyridyl complexes.

163. Formation of Fuel via Photochemical Electron Transfer

G. Jones **$102,000**
Department of Chemistry

This research will investigate photochemical electron transfer reactions that are potentially useful in photoformation of fuel or useful chemicals. New reagents are under development that would permit the separation of oxidation and reduction components through temporary storage of redox equivalents in stable photoproducts. Novel sulfur heterocycles capable of two-electron oxidation are of particular interest as electron relays for experiments involving electron transfer in solution. Studies also encompass photoinduced electron transfer reactions of organic dyes that are bound to water soluble polymers. Applications of electron transfer in photochemical decomposition of hydrogen sulfide, hydrogen halide, and water are under consideration. Investigations include study of the photochemistry of charge-transfer complexes or ion-pairs and factors affecting the yield of photoinduced electron transfer including changes in medium, charge-type, and steric requirements.

Brandeis University
Waltham, Massachusetts 02254

164. Photochemical Reactions of Complex Molecules in Condensed Phase

H. Linschitz **$96,800**
Department of Chemistry

The purpose of this project is to identify and evaluate factors governing the efficiency of primary radical formation in photochemical redox reactions. This is a general problem in photochemical energy conversion since charge-transfer kinetic intermediates may lead either to radical products or dissipative quenching. Primary excited-state reaction rates and radical yields are measured by laser flash photolysis on simple systems in solution, using aryl ketones or porphyrins as substrates, with a variety of redox reagents including water. Reduction of triplet ketones by inorganic anions is studied as a function of anion redox potential, concentration, and solvent. Primary yields that increase strongly with concentration may be correlated with spin-orbit interactions within the anion radical ($X\cdot$ or $X_2\cdot^-$) components of the charge-transfer reaction complex. Marked medium effects possibly related to the strength of the solvent cage also occur. As models of photosynthetic reaction centers, the thermodynamic, spectroscopic, and photochemical properties of porphyrin aggregates and ligand complexes are also studied. Porphyrin dimers containing two different complexed metals form radicals with high quantum yields.

Brown University
Providence, Rhode Island 02912

165. A Unified Approach to Characterization of Collisions Between Reactive Radical Pairs in Solution

R.G. Lawler **$34,300**
Department of Chemistry **(15 mo.)**

A project is underway to systematically characterize the reactive and unreactive encounters between simple organic and inorganic free radicals in aqueous and organic solvents using electron paramagnetic resonance (EPR). A unique flow system for studying radicals produced by electron radiolysis has been constructed and applied to measurements of Heisenberg spin exchange rates for a series of radicals derived from simple acids and alcohols. It is found that even those radicals that react at diffusion controlled rates also exhibit (through the presence of spin exchange) evidence for unreactive encounters. Electron relaxation times for this series of radicals have also been measured with high accuracy for the first time. It is found that the spin-rotation mechanism provides the only satisfactory explanation for the unexpected short observed relaxation times. Comparison of chemical decay and spin exchange rates for a series of nearly stable radicals has also been undertaken using CW EPR and optical detection methods.

University of California
Irvine, California 92717

166. *Research in Chemical Kinetics*
F.S. Rowland **$192,000**
Department of Chemistry

This project focuses on understanding the rates and mechanisms of chemical reactions, including some of interest to atmospheric chemistry. The reactions of thermalized ^{18}F and ^{38}Cl atoms with gaseous $(CH_2{=}CHCH_2)M$ compounds are being studied for M = tin, germanium, silicon, carbon to determine the extent of restricted intramolecular energy flow (non-RRKM) in such systems. Reactions of halogen atoms with haloolefins ($X + CH_2 = CHY$; X = fluorine, chlorine; Y = fluorine, chlorine, bromine, CH_2Cl) are furnishing rate information about radical lifetimes, and mechanistic information such as selectivity and isomerization. The temperature dependence of ^{38}Cl reactions with olefins is being studied over the 240 to 360 K temperature range. The mechanism of the direct gas-phase photolysis of $^{14}CS_2$ is being investigated with and without O_2 present. The rates and mechanisms of hydrolysis in aqueous solution are being measured for gases occurring in the atmosphere, including OCS, CH_3I, and CH_3Br. The gas phase photolyses of PH_3 and P_2H_4, and the co-photolysis of PH_3 and NH_3 are being investigated. The possibility of hot chlorine abstraction by energetic ^{38}Cl atoms is being tested. The thermalization of energetic tritium atoms in collisions with krypton and CF_4 is being studied using the additional reaction with C_2H_4 as the monitor.

167. *Single-Collision Studies of Hot Atom Energy Transfer and Chemical Reaction*
J.J. Valentini **$77,600**
Department of Chemistry

This project involves the study of the dynamics of reactive and inelastic (energy transfer) collisions of translationally hot hydrogen, deuterium, and oxygen atoms. The hot hydrogen, deuterium, and oxygen are produced by pulsed-laser photodissociation of appropriate precursors (e.g., HI and DI for hydrogen and deuterium atoms, and O_3 for oxygen atoms). The reactive and energy transfer collisions of these translationally hot species with molecules like N_2, O_2, CO, CO_2, NH_3, CH_4, CF_4, and SF_6 are being investigated. By variation of the hot atom precursor and the wavelength of photolysis of the precursor, we select the hot atom translational energy in the range of a few tenths to several eV. We measure the rotational and vibrational distributions of the reactive or energy transfer product under single-collision conditions using highly time-resolved coherent anti-Stokes Raman scattering spectroscopy. These measurements yield the state-to-state cross sections for the hot atom collisional processes, and by simple calibration procedures, the total cross sections as well. The objective of this research is to elucidate the dynamics of hot atom collisions, and to contribute to the development of theoretical models of these processes.

University of California
Los Angeles, California 90024

168. *Time-Resolved Laser Studies on the Proton Pump Mechanism of Bacteriorhodopsin*
M.A. El-Sayed **$110,000**
Department of Chemistry and Biochemistry

Bacteriorhodopsin (BR) is another photosynthetic system besides chlorophyll. While chlorophyll uses electron pump, BR uses proton pump. The understanding of storing solar energy via proton pumps is of vital importance. Thus the understanding of the primary photochemical and photophysical process in BR is of vital current interest. We developed time-resolved resonance Raman and optical techniques in order to record the spectra of the different transients formed following the initial photosynthetic absorption process. We attempt to answer questions such as: (1) does energy migration take place to specific sites prior to photochemistry; (2) does isomerization of retinal take place on the picosecond time scale; and (3) how does the Schiff base lose its proton during the photochemical cycle. We recently started using time-resolved optical spectroscopy of the protein and retinal systems to identify the nature of coupling between these two systems, which is undoubtedly responsible for the proton pumping required for photosynthesis in bacteriorhodopsin.

University of California
Santa Barbara, California 93106

169. *Energy Transformations in Organometallic Complexes*
R.J. Watts **$143,000**
Department of Chemistry

This project explores basic photochemical and photophysical phenomena in transition metal complexes. The primary areas of endeavor include: (1) photochemical and photophysical consequences of metal-carbon bonding to acceptor ligands with extended π-systems; (2) electronic relaxation phenomena between excited states of metal complexes; (3) mechanisms of excited state electron transfer reactions; (4) tuning of electronic excited states by extension of π-conjugation in N-heterocyclic ligand-metal complexes; and (5) photochemistry and photophysics of organometallic sandwich complexes. Techniques being applied in these projects include time-resolved emission spectroscopy, laser-induced transient and excited state absorption spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy. Laser double resonance techniques are presently being developed with newly acquired excimer/dye lasers for the purpose of characterizing electronic relaxation between excited states of metal complexes. Synthesis and characterization of complexes containing metal-carbon bonds are being carried out in order to facilitate the projects in area (1) above. The emission spectroscopy and photoinduced electron-transfer reactions of several of these complexes show them to be powerful photoreducing agents. Their participation in photoinduced electron-transfer reactions that are highly endergonic are presently under investigation.

Clarkson College of Technology
Potsdam, New York 13676

170. *Photochemical Solar Energy Conversion in Surfactant Vesicles*

J.H. Fendler	**$155,000**
Department of Chemistry	**(24 mo.)**

Utilization of surfactant vesicles for solar energy conversion continues to be the goal of this project. Our research has centered on the use of vesicles and polymerized vesicles for the *in situ* generation of catalyst-coated colloidal semiconductors and on their employment in efficient solar hydrogen generation. Compartmentalization of appropriate precursors in controlled concentrations has led to the reproducible formation of small catalyst-coated uniform semiconductors in the vesicles. Subsequent to band-gap excitation, undesirable electron hole back recombination has been observed to diminish in the unique microenvironments provided by the vesicles. The most efficient photosensitized water reduction, 8% efficiency, has been accomplished by using polymerized vesicle-entrapped rhodium-coated CdS and benzylalcohol as electron donor. Current research will elucidate and optimize the mechanism of this system.

Clemson University
Clemson, South Carolina 29631

171. *Intramolecular Energy Transfer Reactions as a Method for Metal Complex Assisted Production of Hydrogen*

J.D. Petersen	**$135,500**
Department of Chemistry	**(24 mo.)**

The current research effort concentrates on coupling highly absorbing metal centers to potentially photoactive metal centers (e.g., metal dihydrides) by covalent bonding through bridging ligands. This is done in order to use low energy light to drive useful chemical reactions by intramolecular energy transfer processes. Energetically, this process has been proven feasible. Irradiation of a visible-light absorbing iron complex at 577 nm in the presence of a non-absorbing cobalt-dihydride complex leads to sensitization and the formation of molecular hydrogen. Current efforts are concentrating on covalently coupling the iron and cobalt systems. Additional studies involve the preparation of a new, highly-absorbing, photoluminescent metal center, $Ru(dpp)_3{}^{+2}$, where dpp = 2,3-bis(2-pyridyl)pyrazine. The complex has the possibility of coordinating additional metal centers through remote chelate sites on dpp.

University of Colorado
Boulder, Colorado 80309

172. *Chemical Probes of Charge Transfer at Semiconductor-Liquid Junctions*

C.A. Koval	**$63,600**
Department of Chemistry	

Fundamental aspects of heterogeneous charge transfer kinetics at certain semiconductor-solution interfaces will be investigated with the ultimate goal of improving efficiencies and lowering costs of devices based on photoelectrochemical cells. Electron transfer processes at p-InP electrodes of high to moderate doping density were investigated by monitoring the cyclic voltammetric (CV) dark currents of a series of metallocenes in acetonitrile solutions. The formal reduction potentials of ($E^{o\prime}$) of the metallocene +/0 couples span the band gap of InP, allowing a comparison of the CV responses as a function of $E^{o\prime}$ and the energetic condition of the electrode surface. The energetic condition of the electrode surface during the CV experiments was monitored by measurements of the capacitance of the space charge region. CV behavior at InP was dependent on three factors: (1) the doping density of the electrode, (2) the formation of surface oxide during the experiment, and (3) the proximity of $E^{o\prime}$ to either the conduction or valence band edge.

Columbia University
New York, New York 10027

173. *Laser-Enhanced Chemical Reaction Studies*

G.W. Flynn	**$95,000**
Department of Chemistry	

This project is a study of chemical reactions of laser-pumped molecules, with particular emphasis on the role of vibrational energy transfer processes in chemical dynamics. Fast hydrogen, chlorine, and deuterium atoms are produced by pulsed excimer laser photolysis of gaseous diatomic molecules. These medium-hot atoms cause vibrational excitation of stable molecules during collisions, or react chemically to form products inaccessible to thermally cold species. An infrared diode laser probe technique developed specifically for this project is being employed to monitor, with a resolution of milliwavenumbers, the precise vibrational and rotational states excited during such collisions. The extraordinary resolution of this probe method provides previously unavailable details and insights concerning fundamental combustion, photochemical, and collision processes. Chemical reactions between CO_2 and hot hydrogen atoms, between CO and OH, and between CO_2 and oxygen atoms are being investigated, along with photodissociation of small organic acids.

Dartmouth College
Hanover, New Hampshire 03755

174. *Photoexcited Charge Pair Escape and Recombination*

C.L. Braun	**$40,700**
Department of Chemistry	

The escape and recombination of charge pairs produced by photoexcitation of organic molecules is being studied. The recombination of geminate charge pairs formed by the photoionization of solute molecules in low dielectric constant solvents is found to occur in picoseconds. This process is being studied by pump-probe conductivity techniques. Picosecond absorption measurements of the recombination kinetics are planned. The data are being compared with a detailed theory of the diffusive recombination of geminate charge pairs. The second key goal is to understand the mechanism of charge pair escape in electronically excited electron-donor-acceptor materials. A number of donor-acceptor geometries are being explored in these solid state studies. The possible role of the lowest-energy, charge transfer state in the formation of separated charge pairs (current carriers) is of special interest. Steady-state and nanosecond pulse measurements of both photocurrents and fluorescence are being used to test mechanistic ideas.

University of Florida
Gainesville, Florida 32611

175. Radiation Chemistry of Hydrocarbon and Alkyl Halide Systems
R.J. Hanrahan **$75,000**
Department of Chemistry

Work in the Radiation Chemistry Laboratory at the University of Florida is directed towards understanding the mechanism of product formation in the gamma or pulsed electron radiolysis of simple chemical systems. Measurements are being made on the rates of reaction of OH free radicals with aliphatic and aromatic hydrocarbon gases, as well as with simple hydrocarbons. The work will be expanded to include measurements at elevated temperatures, and to examine other transients in similar systems. An investigation of the radiolytic oxidation of propane has shown many similarities to thermal oxidation, in both products and reaction pathways. It is planned to extend the work to normal and isobutane, and to include measurements above room temperature. Experiments are being initiated to reexamine the classical iodine tagging experiments of Gevantman and Williams, using non-labeled iodine with separation of products via flame ionization gas chromatography. Studies of the radiolysis of H_2-CO mixtures on alumina surfaces (including the effects of temperature, pressure, and addition of finely divided nickel) have shown some interesting results. G values for methane formation greater than 300 have been observed in certain cases.

University of Houston
Houston, Texas 77004

176. Charge Separation in Photoredox Reactions
L. Kevan **$195,000**
Department of Chemistry **(24 mo.)**

The objective of this research is to probe the molecular mechanistic and structural aspects of charge separation in photoredox reactions in micellar and vesicle systems in order to eventually couple this charge separation to chemical energy storage. Tetramethylbenzidine has been photoionized to produce the cation radical in liquid and frozen micellar solutions of anionic, cationic, and nonionic surfactants, and in liquid and frozen synthetic, anionic, and cationic vesicle solutions. The cation is observed by optical absorption, electron spin resonance, and electron spin echo spectrometry. Cation-water and cation-surfactant interactions, detected by electron spin echo modulation analysis, with specific deuteration indicate how the surfactant conformation and the nature of the counterion affect the photoionization efficiency. Micelle surface modification by added salts and varying counterions has led to some control of photoionization efficiency. The decay kinetics of photoproduced cations in micelles have been found to be characterized by time-dependent rate constants and have been described theoretically and tested experimentally.

University of Kansas
Lawrence, Kansas 66045

177. Molecular Design Principles for Biomimetic Solar Energy Conversion Systems
G.M. Maggiora **$96,400**
Departments of Chemistry and Biochemistry

Ab initio quantum mechanical and empirical potential function procedures are being applied in an investigation of the physicochemical factors underlying biological and biomimetic solar energy conversion. These factors will be used to develop a set of molecular design principles that will enable chemists to more efficiently formulate structures of potential biomimetic photoconversion systems possessing specified properties. Current studies are directed toward porphyrin dimer and trimer systems, especially hetero-dimers. Preliminary results indicate the existence of low-lying, nonradiative charge-transfer states in magnesium porphine-porphine dimers, which may be sufficiently long-lived to facilitate electron transfer from these dimers to appropriate acceptors. Further evaluation includes the effects of intermolecular geometry and microenvironment on the location and character of the charge-transfer states. Studies are also continuing on the evaluation of possible molecular candidates for the P700 and P680 photoactive species in the photoreaction centers of green plants. Development of new and improved theoretical methodologies and algorithms are being actively pursued.

Louisiana State University
Baton Rouge, Louisiana 70803-0301

178. Theoretical Studies of Electron and Proton Transfer Processes in Fluids
N.R. Kestner **$120,000**
Department of Chemistry **(24 mo.)**

This research project is designed to study electron and proton transfer processes in fluids, especially those which could be important in energy conversion. General theoretical studies are probing the role of temperature, pressure, and solvent effects on electron transfer rates. Our special attention is directed to such effects for reactions in the abnormal, or highly exothermic regions. Related work is exploring structure-activity relations, which are important in the related proton transfer processes. The general theories are being applied to specific reactions. In this regard, we are determining very accurate water-water interactions and other intermolecular potentials, exploring in detail the role of basis set errors. These are being used to obtain accurate interaction energies between electron transfer species such as iron(II) and iron(III) in aqueous solutions. Other studies are directed at predicting electron transfer rates in glasses and highly viscous media.

University of Massachusetts
Boston, Massachusetts 02125

179. Investigation of the Structure of Photosynthetic Reaction Centers
H. van Willigen **$69,500**
Department of Chemistry

The structure of photosynthetic reaction centers and model systems is studied with the aid of magnetic resonance techniques and optical spectroscopy. A spectroscopic investigation of dimerization of some water soluble porphyrins was made to get an insight into the relation between dimer structure and spectroscopic characteristics. The photoexcited triplet state P^T of *Rhodopseudomonas sphaeroides* R-26 has been investigated using ENDOR measurements on frozen solutions of the photosynthetic reaction centers. Hyperfine data derived from the ENDOR spectra of P^T are compatible with a model that assumes the triplet state is delocalized over two bacteriochlorophyll *a* molecules.

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

180. Photochemical Energy Storage: Studies of Inorganic Photoassistance Agents

M.S. Wrighton **$240,000**
Department of Chemistry

Light-driven, energy-storing chemical reactions are the object of study in this research project. Emphasis is on the use of chemically derivatized semiconductor electrodes as the photoassistance agents for redox reactions such as the oxidation and reduction of H_2O. Fundamental studies of the nature of semiconductor-electrolyte interfaces to establish the energetics and kinetics for light-driven redox processes are one aspect of the project. Another aspect is chemical derivatization of the semiconductor surface for the purpose of improving durability and kinetics for the desired redox reaction. In the area of electrocatalysis, surface modification with metals, oxides, and polymers is being studied. Catalysis of halide oxidation and H_2O reduction have received most attention. Catalytic materials include noble metals, oxides, and molecular catalysts. Exploratory studies to find unique interactions of redox reagents with semiconductor electrode surfaces, such as S-donors with II-VI semiconductors, are in progress. Such unique interactions lead to high efficiency for energy conversion and specific redox processes.

University of Minnesota
Minneapolis, Minnesota 55455

181. The Contribution of Electronically Excited States to the Radiation Chemistry of Organic Systems

S. Lipsky **$160,000**
Department of Chemistry

We study photophysical properties of organic molecules that have relevance in determining their radiation-chemical behavior. Significant recent advances include: (1) demonstration of the experimental and theoretical validity of a new and improved empirical form for the dependence on scavenger concentration of the efficiency of quenching geminate-ion recombination fluorescence in irradiated hydrocarbon liquids; (2) observation and quantification of the effect of a scavenger to reduce the average range of an electron photoejected from a solute in a non-polar liquid via their interaction prior to electron thermalization; (3) a more reliable determination of the yields of excited states of selected solutes in aromatic as compared with saturated hydrocarbon solvents; and (4) the observation and quantitative analysis of a non-diffusional transfer of solvent positive charge to a positive ion scavenger in irradiated saturated hydrocarbon liquids.

Mount Holyoke College
South Hadley, Massachusetts 01075

182. The Study of the Photochemistry of Organic Dyes at Semiconductor Electrodes Using Total Internal Reflection Techniques

M.T. Spitler **$65,300**
Department of Chemistry **(24 mo.)**

The photochemistry of organic dyes adsorbed at semiconductor surfaces is being studied through a combination of photoelectrochemical and total internal reflection techniques. The utilization of an attenuated total reflection method enables an *in situ* determination of the quantum efficiency of current producing photoreactions. The photochemistry of dyes at ZnO, TiO_2, and $SrTiO_3$ single crystal surfaces is being investigated using dyes that show significant triplet character or tendency to form aggregates. Selected photoreactions will also be studied at surfaces chemically modified in differing regions of donor and acceptor to serve as a model for catalytic photoreactions at powders.

National Bureau of Standards
Gaithersburg, Maryland 20899

183. Support of Critical Data Compilations

D.R. Lide, Jr. **$150,000**
Office of Standard Reference Data **(CS Part)**

The Office of Standard Reference Data of the National Bureau of Standards administers a collaborative interagency program for the preparation of compilations of physical and chemical reference data. Current projects within the scope of the Division of Chemical Sciences fall in the following areas: physical and thermodynamic properties of fluids, solubility, electrolyte properties, gas-phase chemical kinetics, hydrocarbon properties, atomic data relevant to fusion, and thermodynamics of high-temperature systems. The approach is to review critically all relevant data from the literature, compare with theory, and select the most reliable values. Whenever possible, correlations are developed which allow prediction of unmeasured properties. Reviews are in press on high-temperature vaporization of alkali metal oxides, nucleation limits of liquids, thermodynamic properties of alkylbenzenes, and other topics.

184. Pulse Radiolytic Studies of Inter- and Intramolecular Electron Transfer Processes

P. Neta **$140,000**
Center for Chemical Physics

Studies of both intermolecular and intramolecular electron transfer processes are conducted using pulsed electron sources to generate the reactive intermediates, and time resolved absorption spectrophotometry to follow the kinetics of the ensuing reactions. Quantitative results are obtained detailing the effects of structural parameters on the rates of intramolecular electron transfer within radical anions. In particular, intramolecular electron transfer reactions within covalently bound dimeric viologens and metalloporphyrins are studied because of the importance of these molecules in artificial photosynthesis and because they allow detailed analysis of the effect of driving force and structural parameters on the rates of these processes. The mechanism and thermodynamics of intermolecular electron transfer reactions are studied, using measurements of rate and equilibrium constants as a function of temperature to obtain quantitative information about activation energies, enthalpy, and entropy changes associated with these processes. Comparison of values of liquid and gas phase systems will permit a more quantitative understanding of solvation effects in electron transfer processes. Bimolecular electron transfer reactions of metalloporphyrins and their anion- and cation-radicals with a variety of other chemical systems, and especially with certain metal catalysts, are being studied as models for understanding artificial photosynthesis and other photochemical processes involving porphyrins.

University of Nebraska
Lincoln, Nebraska 68588-0304

185. Electrochemical and Optical Studies of Model Photosynthetic Systems

T.M. Cotton **$75,000**
Department of Chemistry

A combination of electrochemical and resonance Raman techniques, supplemented by ultraviolet visible spectroscopy, is being used to characterize some important properties of the pigments of the bacterial photosynthetic reaction center. Characterization includes determination of the redox states of the various components during the initial photoact as well as the identity and spectral character of the neutral and charged species involved. Much of the present knowledge of the primary photoact in photosynthesis is based on *in vitro* or *in vivo* measurements, which are subject to ambiguous interpretation. The present approach uses innovative techniques in an attempt to overcome some of the drawbacks of previous studies. Attempts are underway to incorporate bacteriochlorophyll, bacteriopheophytin, and quinones from reaction centers into monolayer arrays. In these designed monolayer constructions the orientation, spacing, and identity of the included components are under a high degree of control. Electrochemical and spectral studies of the monolayer systems should provide new insights regarding the effect of structure on the optical and redox properties of these molecules.

186. Energetics of the Formation and Reactions of Gaseous Ions

G.G. Meisels **$85,000**
Department of Chemistry

The project focuses on two activities: (1) threshold photoelectron-coincident photon mass spectrometry used to study ions whose internal energies are known within 0.025 eV and (2) a mass spectrometer with a pulsed high-pressure ion source and uniform fields used to derive the spatial distribution of ionization by 100 to 1000 eV electrons, and the thermalization times and distances of such electrons from ion residence times. In the first activity, the energetics of the formation, isomerization, and fragmentation of gaseous cations are measured. Nitrobenzene dissociation is described best by a model that involves direct dissociation and isomerization of the phenyl cation to a linear structure before fragmentation. In the second activity, the energy loss of electrons by collisions in 1 torr helium leads to formation of SF_6^- after electrons thermalize, a process that has a half life of about 3 μs. Linear ionization rates in hydrocarbon gases derived from arrival-time distributions of dominant, long-lived positive ions and of negative ions produced by capture of thermalized electrons lead to electron ranges that are somewhat larger than those derived from bulk ionization rate measurements. This reflects the differences between collection geometries of these experiments.

187. High-Energy Halogen Reactions Activated by Nuclear Transformations

E.P. Rack **$72,900**
Department of Chemistry

The functional goal of this project is to understand better the chemical reactivity of high-energy monovalent species. High-energy reactions of halogen atoms or ions activated by nuclear transformations are studied in gaseous, high-pressure, and condensed-phase saturated and unsaturated hydrocarbons, halomethanes, and liquid and solid aqueous solutions of biological molecules. Specifically, the stereochemistry involving single chiral center molecules, systematics, mechanisms, and halogen reactivity in a collapsing molecular environment, and caging of hot atoms in an ice lattice are under investigation. The stereochemistry of exothermic halogen atom homolytic bimolecular substitution (${}^{S}H^{2}$) at the chiral centers of chiral 2-halopropionyl halides is currently studied. Practical applications of recoil atom chemistry to activation analysis or molecules in biological or environmental systems, to radiopharmacy involving synthesis and radioprotection, and to the study of solute-solute and solute-solvent interactions of dilute aqueous solutions of methyl halides and biological molecules are being carried out.

University of North Carolina
Chapel Hill, North Carolina 27514

188. Energy Conversion Processes Based on Molecular Excited States

T.J. Meyer **$105,000**
Department of Chemistry

This research effort is based on the study and exploitation of excited states of transition metal complexes. A particularly important goal is the design and characterization of new classes of photosensitizers, and their application to solar energy related problems. In technical detail the work involves the measurement of the photochemical and photophysical properties of excited states, the application of theory to such processes, synthesis of new types of potential photosensitizers, the preparations and properties of metallopolymers containing metal complex chromophores, the study of electron and energy transfer processes of the photosensitizers in solutions and polymeric films, and possible applications of these materials in photochemical and photoelectrochemical energy conversion processes.

University of North Carolina at Charlotte
Charlotte, North Carolina 28223

189. Oligomer and Mixed-Metal Compounds, Potential Multielectron Transfer Catalysts

D.P. Rillema **$63,200**
Department of Chemistry

The goal of the project is to design and characterize new classes of photosensitizers and their application to solar energy conversion. Current work involves characterizations of fundamental precursors that will be used (1) to prepare molecules that contain a coordinatively unsaturated metal complex connected to a photoactive electron transfer metal chromophore and (2) to synthesize multi-metal complexes capable of "simultaneous" multielectron transfer. The characterizations include: (1) isomer separation of metal complexes containing asymmetric ligands; (2) thermodynamic studies of ground state and excited state redox properties; (3) assessment of the relative energy positions of heterocyclic ligand π^* energy levels and their exploitation for the preparation of new light-sensitive chromophores; and (4) photophysical investigations of the excited state energies, lifetimes, and electron transfer properties of the photochromophores.

Oregon Graduate Center

Beaverton, Oregon 97006-1999

190. Fundamental Studies in Charge Separation at Interfaces in Relation to Water Photolysis

J.K. Hurst **$80,000**
Department of Chemical, Biological and Environmental Sciences

This project aims to improve our conceptual understanding of the influence of microphase separation and compartmentation upon oxidation reduction processes. Two redox systems have been developed that exhibit apparent electron exchange between components bound at the opposite vesicle interfaces. For the amphiphilic $(NH_3)_5Ru$-4- (11′-dodecenyl) pyridine$^{+3/+2}$ ion, transmembrane redox across phospholipid liposomes appears to occur by rate-limiting electron tunneling. Evidence was obtained in preliminary studies suggesting that N-alkyl-N′- methylbipyridinium$^{+2/+}$ ions also undergo transmembrane electron exchange across dihexadecylphosphate (DHP) vesicles: (1) ferricyanide ion occluded within the inner aqueous phase effectively quenches photoredox-generated viologen radical formed on the outer surface, but only when viologen is bound to both surfaces and (2) chemical reduction by externally added dithionite ion is biphasic in character. Our recent, more complete study of oxidative quenching of zinc(II) porphyrins and chemical oxidation of several reductants by DHP-bound viologens has shown that these reactions are far more complex than previously realized. In particular, viologen aggregation gives rise to formation of reactive patches as consequence of attendant favorable electrostatics at these sites. This phenomenon greatly complicates both interpretation of experimental data and theoretical modeling in these types of systems. The establishment of conditions for observing transmembrane electron transfer in these reactions is significant because they are particularly amenable to structural permutations that will allow identification of the major factors controlling transmembrane charge transfer.

Pennsylvania State University

University Park, Pennsylvania 16802

191. The Free-Radical and Ion Chemistry of Volatile Silanes, Germanes, and Phosphines

F.W. Lampe **$80,000**
Department of Chemistry

This research project consists of experimental studies of the chemical reactions initiated by the irradiation of gaseous silanes and germanes with electrons, infrared laser radiation, and vacuum ultraviolet light. From the experimental studies, fundamental reaction mechanisms relative to this new and unexplored chemistry are developed. In particular, the knowledge and understanding developed enables us to attempt useful exploitations of photochemical and radiation chemical techniques for the synthesis of amorphous solids of silicon, germanium, and mixtures thereof. Presently under study is the infrared laser photochemistry of CH_3SiH_3, and SiH_4-NO, SiH_4-GeH_4, and SiH_4-CH_3Cl mixtures; the vacuum ultraviolet photochemistry of GeH_4 and SiH_4-GeH_4-NO mixtures; and the ion chemistry of SiH_4-CH_3Cl, SiH_4-CH_2Cl_2, SiH_4-$CHCl_3$, SiH_4-CCl_4, and CH_4-HCN mixtures.

Princeton University

Princeton, New Jersey 08544

192. Surface Chemistry at the Semiconductor Electrolyte Interface

A. Bocarsly **$72,000**
Department of Chemistry

This study encompasses the role of surface chemistry in photodecomposition processes occuring at the II-VI semiconductor-electrolyte interface. Both anodic and cathodic decomposition channels are of interest. Of particular concern is the effect of interfacial overlayers formed from decomposition products on the overall chemistry and behavior of the cadmium chalcogenide-based photoelectrochemical cell. Such layers may add an element of stability to the photoactive interface. The presence of unexpected interfacial species also opens up the possibility of novel energy storage schemes based on semiconductor decomposition products.

193. Photoelectrochemistry with Chemically Modified Electrodes

T.G. Spiro **$186,000**
Department of Chemistry **(24 mo.)**

The electrochemistry and photoelectrochemistry of metalloporphyrin electrode films are being explored, with a view toward catalyzing useful energy storage reactions, including the splitting of water to H_2O_2. Stable metalloprotoporphyrin films have been prepared via electroinitiated polymerization of the vinyl side-chains, and other porphyrin polymerization schemes are being explored. Cobalt porphyrins are being applied to the catalysis of H_2 production from water. The kinetics of the catalysis have been investigated in homogeneous solution using electrochemical techniques. Cobalt porphyrin electrode films capable of sustained H_2 production have been developed, and their characteristics are being explored. Iron, chromium, and manganese porphyrins are being explored in oxidative chemistry, with the eventual aim of catalyzing water oxidation.

University of Puerto Rico

Mayaguez, Puerto Rico 00708

194. Photoelectrochemistry of New Phenothiazine Dye Derivatives

F.A. Souto **$45,000**
Department of Chemistry

The project objective is to assess the potential of functionalized redox dyes as simple models of more elaborated compounds that could mediate more efficiently direct conversion of photons into electrons with artificial photosynthetic systems. Emphasis is on experimental evaluation of the photophysical, photochemical, and electrochemical processes involved in the electron-transfer quenching of excited amphiphilic thionines in isotropic aqueous acid electrolytes and in anisotropic surfactant assemblies (e.g., micelles). The properties of thionine and its 2,6- and 4,6-disulfonated and 2,4,6-tri-sulfonated analogs are examined using the techniques of steady-state electronic absorption and emission spectrophotometry, fluorescence time decay in the subnanosecond time regime (first excited singlet), flash photolysis in the microsecond time regime (first excited triplet state), rotating disc electrode, rotating optical disc ring electrode, and stopped-flow electrochemical kinetics. These experiments are helping establish the influence in the efficiency of photochemical energy conversion of the structural characteristics around the active chromophore and of the amphiphilic balance between redox dye and surrounding environment. Current studies with the named derivatives of thionine indicate that the study of such compounds has potential to advance current knowledge on photochemical redox mediation in natural and artificial energy conversion systems.

Purdue University
West Lafayette, Indiana 47907

195. *Study of the Motion of Electrons in Non-Polar Classical Liquids*

G. Ascarelli **$70,000**
Department of Physics

We have calculated the mobility of electrons injected in liquid argon assuming scattering due to density fluctuations (square wells and barriers). A density fluctuation Δn in a spherical volume v has probability $[\exp - (\Delta n)^2 v/2S(0)]\,[\exp - r/\xi]$ where S(0) is the structure factor at zero momentum and ξ the correlation length. Partial waves were calculated up to $l=4$ for the case when either one of the factors was larger than 10^{-6}. It is noteworthy that as long as the minimum value of v considered above is sufficiently small, no mobility maximum appears when the total ΔV_0 that corresponds to a given Δn is considered; reasoning is that the corresponding density fluctuations are not small. This is to be contrasted with a perturbation calculation based on the Born approximation. From the above results and the phonon scattering calculated previously it becomes clear that both mechanisms provide comparable contributions to the mobility. The experimental structure for measurements in argon had to be extensively modified to increase the electric field homogeneity in the metal enclosed cell. New ways of measuring the density, pressure, and temperature of the sample as well as the temperature gradient across the sample were introduced to eliminate large experimental errors.

University of Rochester
Rochester, New York 14627

196. *Picosecond Studies of Charge Transfer at Semiconductor Liquid Junctions*

R.J.D. Miller **$75,000**
Department of Chemistry **(11 mo.)**

The advent of efficient semiconductor liquid junction solar cells provides an excellent system for *in situ* spectroscopic studies of the electron or hole (charge) transfer process at solid-liquid interfaces. The ultrafast kinetics of the interfacial transfer process are not well understood. To date, there have been two proposed mechanisms for the photoinduced charge step: (1) tunneling processes across the space charge region (Helmholtz barrier) and (2) thermally equilibrated charge scattering from the surface. The predicted time course for these two mechanisms is (respectively) ~100 fsec and > 10 psec. Two techniques, picosecond holography and a proposed new method of electro-optic sampling, will be used to optically study the photoinduced charge transfer process directly at the semiconductor-liquid interface. The observables of the two techniques are the charge transfer rate (via the minority carrier lifetime) and the temporal behavior of the electric field across the space charge region, respectively. Both techniques have adequate temporal resolution (~100 fsec) and sensitivity to distinguish on the basis of the observed time scale, which mechanism, if either, is operating for a particular system. Studies will focus on understanding the effect of the depletion layer width and the effective mass of the minority carrier on the charge transfer dynamics.

197. *Applications of Photo-Induced Electron Transfer and Hydrogen Abstraction Processes to Chemical and Electrochemical Conversion Processes*

D.G. Whitten **$190,000**
Department of Chemistry **(24 mo.)**

This research project involves studies of photochemical redox reactions occurring via electron transfer, hydrogen atom abstraction processes, and C–C bond cleavage initiated by excitation of chromophores absorbing visible and near ultraviolet light. A part of the project involves direct study of photochemical reactions and external factors that can modify them. In addition, photoelectrochemical processes based on them are being investigated. Our studies of direct photochemical reactions have recently focused on photoredox reactions of certain indigo dyes. These dyes undergo net photoreduction processes with a variety of electron donors by, in some cases, a multiplicity of mechanisms. Among the most interesting mechanisms is a net hydride ion transfer that occurs via a sequence of electron, proton, and second electron transfer, all within the initially formed encounter complex. We are also investigating the effect of inclusion complex formation on reactivity using various amylose derivatives as selective hosts for a variety of reactive substrates.

Stanford University
Stanford, California 94305

198. *Energy Transfer Processes in Solar Energy Conversion*

M.D. Fayer **$112,045**
Department of Chemistry

This project examines energy transport processes in nontraditional systems using picosecond and other optical techniques and statistical mechanical theoretical methods. A wide variety of situations in both natural and man-made systems cannot be modeled as periodic arrays of molecules. In many systems, inherent disorder and characteristic size and shape play key roles in determining energy dynamics. We have developed the first accurate and detailed statistical mechanics theory of energy transport in disordered systems with finite volume. We are using a picosecond transient holographic grating technique and picosecond fluorescence mixing methods with conventional fluorescence and absorption experiments. We are studying energy transport among dye molecules attached to long hydrocarbon chains organized in multibilayer systems and energy transport in chromophore-containing polymers. We have studied excitation transport between chlorophyllide molecules in a protein environment and determined the direction of the chlorophyll transition dipole relative to the molecular framework. In addition, we are studying experimentally and theoretically electron transport in disordered systems. Using picosecond lasers, electron transfer between organic molecules in both excited states and ground states is examined on a time scale fast enough to show the dynamical details important in natural and laboratory chemical electron transfer reactions. Electron transport in amorphous silicon is under investigation with transient grating techniques; we have measured the dynamics of carrier quenching by surfaces.

199. Fundamental Electron Transfer Processes at the Semiconductor-Liquid Interface

N.S. Lewis **$150,000**
Department of Chemistry **(24 mo.)**

Variations in fundamental electron transfer parameters at the semiconductor-liquid interface are studied with systematic changes in bulk semiconductor composition in the $GaAs_{1-x}P_x$ and $Al_{1-x}Ga_xAs$ series of alloys. We have obtained single crystal, epitaxially grown, n-type samples of representative members of these series and have investigated changes in electrode properties in both aqueous and nonaqueous solvents. In aqueous selenide-containing solutions, we observe stable photoanode behavior for all members of the series, and observe high spectral response characteristics for all materials. Similar behavior is found in nonaqueous solvents, and in both solvent systems the photoanode properties seem more strongly correlated to the bulk semiconductor band gap than to the actual bulk or surface composition of the electrode. We have determined the activation parameters for the rate-determining recombination step at n-GaAs/CH_3CN-ferrocene interfaces, and find that plots of open circuit voltage vs. temperature yield activation energies of 1.4 V. A detailed study of the kinetics in this system (performed by systematic variation of minority carrier diffusion length, temperature, dopant density, and photocurrent density) indicates that defect models invoked for pinning of solid state GaAs Schottky barrier systems do not apply to our n-GaAs/liquid interfaces. The relationship of these theories to the chemistry of liquid junctions is being investigated.

University of Tennessee
Knoxville, Tennessee 37996-1600

200. Studies of Radiation-Produced Radicals and Radical Ions

T.F. Williams **$100,000**
Department of Chemistry

The basic objective of this project is to characterize the structure and reactivity of important free radical and radical ion intermediates generated by irradiation of molecular systems. Radical cations are generated under matrix-isolation conditions by γ irradiation of solid solutions of the parent compounds in Freon matrices at low temperatures while radical anions are similarly produced and stabilized in hydrocarbon matrices, the pertinent reactions involving positive hole transfer and electron capture, respectively. Electron spin resonance (ESR) spectroscopy is used to characterize these paramagnetic species. Specific projects include studies of (1) spin delocalization in fluorocarbon and fluorine-containing radical anions, (2) radical cation-Freon solvent σ^* complexes, (3) radical cation rearrangements involving ring opening (oxirane cation) or hydrogen atom transfer (trimethyl phosphate cation), (4) long-range hyperfine interactions in radical cations of carbonyl compound, and (5) ligand structure of organometallic cations derived from Group IVB organometals. Additional work is in progress on the photogeneration of radical ions.

University of Texas
Austin, Texas 78712

201. Organic Redox Phototransformations at Chemically Modified Surfaces

M.A. Fox **$89,000**
Department of Chemistry

Exploratory and mechanistic studies of new chemical transformations of organic molecules at native and chemically modified surfaces represent the goal of this research. New electrode materials are being prepared by adsorption, covalent attachment, polymerization, and mulling with electroactive or light-sensitive materials, and physical studies of the properties of these materials are being conducted. Both photocatalytic and photosynthetic organic reactions can be initiated by electron exchange induced by visible light excitation of either native or chemically modified semiconductor surfaces. Mechanisms for charge migration through polymer layers coating electrodes are being determined. Photophysical characterization of dye-excited states as a function of their micro-environment are being obtained. New metal non-oxides and p-type semiconductors are also being investigated, and the search for new reactions on these novel materials is continuing.

Washington University
St. Louis, Missouri 63130

202. Reaction Studies of Hot Silicon, Germanium, and Carbon Atoms

P.P. Gaspar **$85,000**
Department of Chemistry

The project goal is to determine: (1) the reactions of high-energy silicon, germanium, and carbon atoms; (2) how their reactions take place; and (3) how the reaction pathways are influenced by the energy and the electronic states of the free atoms and of the reactive intermediates that they produce. Silicon, germanium, and carbon atoms are formed at high energies by nuclear transformations such as $^{31}P(n,p)^{31}Si$, $^{76}Ge(n,2n)^{75}Ge$, and $^{12}C(p,pn)^{11}C$, and at low energies by thermal evaporation. Reactive intermediates such as SiH_2 and $SiMe_2$ are generated by pyrolysis and photolysis. The barrier for insertion by a silylene into a carbon-hydrogen bond has been measured for the first time. The mechanism for attack by high-energy carbon atoms on aromatic rings consists of insertion into carbon-hydrogen bonds. The addition of dimethylsilylene to substituted 1,3-dienes is fully reversible, thus providing new ways to generate silylenes and new synthetically useful reactions. Absolute rate measurements on silylene reactions by laser flash photolysis provide important new mechanistic insights.

energy of the molecules and the nature of the surface. The angular distributions of thermal neon and argon atoms scattered nearly elastically from a crystalline surface of LiF shows structure that is obscured when the full range of velocities leaving the crystal is recorded.

University of California
Irvine, California 92717

207. *Laser Studies on Internal State Dependence of Excitation and Deexcitation Processes*
E.K.C. Lee **$109,900**
Department of Chemistry **(18 mo.)**

This research project is designed to measure the state-to-state rates of excitation and deexcitation of small polyatomic molecules in single rotational and vibrational levels of the excited electronic state. Emphasis will be placed on studies of small free radicals and intermediate molecules important to combustion and flame chemistry. The experimental techniques of laser-induced fluorescence spectroscopy and laser-induced photofragment luminescence spectroscopy by one-photon and two-photon absorption will be studied in frequency-domain and time-domain. Search for new electronic states as well as new fluorescence and chemiluminescence channels will be made. Variations in the quantum yields of fluorescence, radiative life-times, molecular perturbations that affect radiative processes, collisional energy transfer rates, and temperature dependence as a function of rotational and vibrational states will be studied experimentally and theoretically.

California Institute of Technology
Pasadena, California 91125

208. *High Resolution Infrared Spectroscopy: Dynamics of Vibrationally Excited States*
K.C. Janda **$68,000**
Department of Chemistry

Molecular beam laser excited fluorescence spectroscopy and laser photodissociation spectroscopy are used to characterize the rate of intramolecular energy redistribution in excited vibrational states of molecules. Van der Waals molecules are used as prototypes for this process because the redistribution of a single quantum of vibrational energy will break the weak bond. It is hoped that a detailed set of physical principles can be developed to describe this process. These principles may then be used to help understand energy redistribution in much more complicated molecules such as those involved in flames. For the past several years we have been observing that energy transfer rates can be a very strong function of structure for molecular complexes that contain ethylene. In one case, NeC_2H_4, the energy transfer is slow enough that we have recorded and analyzed rotational structure. During the past year we have been studying the simple rare gas-dihalogen molecules. For the triatomic molecule $NeBr_2$ a rotationally resolved spectrum was observed and resolved. It is found that while energy transfer rates are a strong function of vibrational quantum number, they are only a weak function of the rotational quantum number.

209. *Studies in Spectroscopy and Chemical Dynamics*
A. Kuppermann **$98,000**
Chemistry and Chemical Engineering Division

Studies are being made on the low energy electron impact spectroscopy of molecules and free radicals of importance in combustion processes. The aim of these studies is to gain information about the low-lying electronically excited spin-forbidden states of these species and of their possible relevance to the reactions occurring in these processes. Studies are also being made on the dynamics of elementary reactions involving free radicals such as H or CH_3. Free radicals are produced by pulsed laser photolysis of a parent halide and an abstraction product of the reaction of the free radical with molecules such as C_2H_2, and HCN is detected by vacuum ultraviolet laser-induced fluorescence, using a second laser time-delayed with respect to the first one. The object of these studies is to obtain information about the translational energy dependence of the cross section of these reactions and its relation to activation energies. Such reactions are important in combustion processes.

Catholic University of America
Washington, District of Columbia 20064

210. *Kinetics and Mechanisms of Key Elementary Processes of Importance to High Temperature Combustion Chemistry*
M.C. Lin, W.A. Sanders **$64,200**
Department of Chemistry

A systematic, multi-thrust study of the kinetics and mechanisms of key elementary chemical processes relevant to high temperature combustion chemistry will be conducted. The project will combine state-of-the-art experimental work with computer modeling and theoretical interpretation of observed kinetic data. The major effort will be concentrated in three areas: (1) shock-tube studies of high-temperature elementary reactions involved in the combustion of benzene and related chemical processes; (2) two-laser pump-probe measurements of high-temperature free radical reaction kinetics, with particular emphasis on processes leading to NO_x formation; and (3) interpretation and extrapolation of low-temperature rate constants for reactions involving long-lived intermediates by means of the RRKM theory.

University of Chicago
Chicago, Illinois 60637

211. *Topics in Finite Time Thermodynamics*
R.S. Berry **$35,600**
Department of Chemistry **(6 mo.)**

The term finite time thermodynamics refers to the extension of traditional thermodynamics to the description of systems and processes whose constraints include finite times or nonzero rates of operation. In particular, the term refers to the determination of the extremal performance and the paths that would yield that performance, when the constraints of finite-time operation must be met. The progress of this group since the last report has included: (1) theoretical description and optimization of a new type of engine, based on a light-driven dissipative progress; (2) further exploration of geometric formulation of thermodynamics based on the metric introduced by Weinhold, including proofs-of-relations between dissipation in a finite-time process

Wayne State University
Detroit, Michigan 48202

203. Dynamics of Charge-Transfer Excited States Relevant to Photochemical Energy Conversion
E.C. Lim **$81,500**
Department of Chemistry

This research addresses basic questions concerning the energetics and dynamics of charge-transfer (CT) excited states that are relevant to photochemical energy conversion. We study CT excited states of electron donor-acceptor (EDA) complexes and transition metal complexes in gas phase and in condensed phase, using laser-based techniques (fluorescence, multi-photon ionization, and so forth). A systematic study of the photophysical properties of EDA complexes containing alkyl benzenes as electron donors reveals that charge recombination is less efficient for D_2A (of sequence DDA) than for DA. Deuteration of methyl hydrogens has relatively large effects on the nonradiative decay rate (k_{nr}) of DA, but only minor effects of k_{nr} of D_2A. The effect of ring deuteration is larger for D_2A than for DA. Results are consistent with the charge delocalization in D_2, which faciliates the charge separation and decreases the magnitude of methyl hyperconjugation. Time-resolved fluorescence indicates that the conformation of DA in the CT excited state is different from that in the ground electronic state. The previous report of the time evolution of fluorescence (attributed to the conformational charge of DA following electronic excitation) has been shown to be due to the association of the electronically excited DA and the ground state D, leading to the formation of electronically excited D_2A. The propensity rule for the intersystem crossing of DA (Lim's rule) and the strong temperature dependence of k_{nr} have been further substantiated. Experiments are presently underway to obtain high-resolution electronic spectra from ultracold gaseous molecules in a supersonic free jet and site-selected molecules in low-temperature matrices.

Chemical Physics

Aerodyne Research, Inc.
Billerica, Massachusetts 01821

204. A Study of CH Reactions Relevant to Combustion-Gasification Processes
J.A. Silver **$92,964**
Center for Chemical and Environmental Physics

Little is known about the reactions of monovalent carbon radicals known as carbynes, and in particular, those of CH radicals. Yet they play an important role in the chemistry of combustion and gasification processes, including the formation of NO_x via the prompt-NO mechanism. They also appear to serve well as a testbed for studying the mechanistic behavior of four-center reactions, and appear to exhibit both abstraction and addition at different temperatures. Our basic research concerns both rate constants and product distributions determined from reactions of CH with other small molecules found in combustion streams. The goal of this project is to improve our fundamental understanding of the chemistry of carbynes. These studies are performed on a high-temperature fast-flow reactor, capable of operating between room temperature and 1500 K. Carbyne radicals are produced by the chemical abstraction reaction of atomic sodium with bromoform or chloroform: $3Na + CHBr_3 \rightarrow CH + 3NaBr$ and detected using laser-induced fluorescence in the 0,0 band of the $A^2\Delta \leftarrow X^2\Pi$ system at 431 nm. We are now investigating the bimolecular reactions of carbyne radicals with hydrogen.

University of Arizona
Tucson, Arizona 85721

205. Chemical Activation of Molecules by Metals: Experimental Studies of Electron Distributions and Bonding
D.L. Lichtenberger **$82,000**
Department of Chemistry

This project focuses on experimental investigation of the electronic structure mechanisms of bond activation of small molecules by transition metals. The primary experimental techniques have been valence helium(I, II), and core x-ray photoelectron spectroscopy of metal-molecule organometallic complexes in the gas phase. Last year, we initiated (1) use of new state-of-the-art instrumentation for photoelectron studies of these molecules on surfaces, (2) development of high-resolution Auger spectroscopy of gas-phase species, and (3) application of synchrotron radiation to these studies. The systems currently receiving most attention involve metal interactions with small organic species that are proposed intermediates in water-gas shift and Fischer-Tropsch catalysis (e.g., alkyls, alkenes, alkynes, methylenes, and vinylidenes). Recent highlights include (1) development of the experimental and theoretical basis of additivity of electronic effects with ligand substitution and of core-valence ionization correlations; (2) establishment of the electronic structure mechanism of early stages of C–H bond activation; (3) comparison of the activation of alkenes and alkynes by electron-rich and electron-poor metals; and (4) characterization of the charge potential demonstrated by early transition metal and high oxidation state systems, with particular application to metathesis and Ziegler polymerization processes.

Brown University
Providence, Rhode Island 02912

206. Interactions of Molecules with Surfaces
E.F. Greene **$69,420**
Department of Chemistry

Studies of the ionization of alkali atoms striking semiconductor surfaces at thermal energies show that phase changes in silicon(111) and (100) surfaces as well as the dynamics of interactions of the surfaces with cesium, potassium, sodium, and lithium may be followed in the temperature range 800 to 1000 K. Similar work with two other semiconductors (SiC and graphite) shows that the atoms find several different kinds of adsorption sites. Experiments with beams of sodium at superthermal energies (up to 100 eV) striking a silicon(100) surface yield more than a 10-fold increase in ionization relative to thermal beams. The rebounding ions leave the surface too rapidly to be neutralized by electrons from the surface to the degree required for the equilibrium achieved at thermal energies. Fast molecules of tetramethydioxetane are activated to react and emit light when they strike surfaces. The yield of light though small (fewer than one photon for 10^8 collisions) depends both on the kinetic and the length of the path for that process calculated by Weinhold's metric; and (3) further extension of the concept of availability (exergy) to processes operating in finite time, and application of this extended concept to extraction of work from a system not initially in internal equilibrium.

212. Laser-Induced Chemical Reactions and Laser-Collision Processes

J.C. Light **$52,000**
James Franck Institute

Laser-induced chemical processes of several types have been observed experimentally. The project objective is to develop theoretical methods to examine these and related processes. Methods to do exact three-dimensional quantum calculations of single photon photodissociation of triatomic molecules have been developed and applied to models of HCN and ICN. A new representation of the problem (discrete variable representation) simplifies the calculation considerably by taking advantage of the localization of the initial state. These techniques are now being applied to the related problems of dissociative attachment in electron molecule collisions ($e^- + F_2$, $e^- + CO_2$) and to dissociation by photoemission from Rydberg states $H_3^*(\text{Rydberg}) \rightarrow H_2 + H + h\nu$. Realistic calculations of multiphoton dissociation of O_3 in intense laser fields are being made using a realistic internal state structure and our recently developed rotating frame transformation. Currently, we are developing an efficient unitary quantum time evolution method for initially localized wave packets in several dimensions. This will be applied to photodissociation and resolvant and Boltzmann operators for polyatomic system.

University of Colorado
Boulder, Colorado 80309

213. Laser Photoelectron Spectroscopy of Ions

G.B. Ellison **$165,000**
Department of Chemistry **(18 mo.)**

Laser photoelectron spectroscopy has been used to study a number of simple negative ions. Our experiments produce direct, reliable thermodynamic information such as electron affinities, radical and ion heats of formation, and bond dissociation energies. These are crucial data required for an understanding of combustion processes. We have completed careful studies of CCO^-, $HCCO^-$, $DCCO^-$, $CH_2{=}CH{-}CH_2^-$, $CH_2{=}CD{-}CH_2^-$, $CD_2{=}CD{-}CD_2^-$, HO_2^-, and DO_2^-.

214. Time-Resolved Studies of Free Radicals and Laser-Initiated Chain Reactions

S.R. Leone **$56,000**
Department of Chemistry

Time and wavelength-resolved infrared emission techniques are used to study free radical production and reactions. Infrared emission spectra have been obtained and analyzed for combusting mixtures of low-pressure chlorine with hydrocarbons. A method has been developed to measure the absolute rate coefficients of methyl radical reactions with molecules such as chlorine, bromine, and hydrogen iodide. Intramolecular vibrational relaxation processes have been observed in the ground electronic state of hydrocarbons by exciting the first CH overtones and detecting the reduction in emission from these states. Laser multiphoton ionization has been used to detect the state distributions of molecular nitrogen. Laser photodissociation of acetone has provided fragment infrared emission spectra of the dissociation products and rates of vibrational deactivation of methyl radicals.

Columbia University
New York, New York 10027

215. Energy Partitioning in Elementary Gas Phase Reactions

R. Bersohn **$70,000**
Department of Chemistry

Elementary atom molecule reactions are being studied by laser-induced fluorescence (LIF), and spectroscopic techniques for detection of atoms are being developed. Isotopic ratios of hydrogen atom products of the reactions $O(^1D) + HD \rightarrow OD(H) + H(D)$ and $S(^1D) + HD \rightarrow SD(H) + H(D)$ were determined to be 1.13 ± 0.08 and 1.93 ± 0.10 respectively. The results are qualitatively in accord with the prediction that in reactions proceeding via a complex (HDO and HDS) the lighter hydrogen atom is more likely to escape. The exchange reaction of photolytically generated hydrogen atoms with D_2O molecules has been observed. Deuterium atoms are seen by LIF when the hydrogen atom has a relative kinetic energy of 54 kcal/mole (dissociated from H_2S at 193 nm), but not when the relative energy is 21 kcal/mole (H_2S at 248 nm). A methyl iodide gas partially dissociated by a 248 nm laser exhibits third harmonic generation near an iodine atom transition at 206.2 nm and near a CH_3I Rydberg transition at 201 nm. This is the first report of third harmonic generation in a molecule with more than two atoms, but the phenomenon is believed to be perfectly general. All molecules should exhibit third harmonic generation just on the high energy side of their Rydberg transitions.

Howard University
Washington, District of Columbia 20059

216. Photolytic Processes for Measurement of Combustion Heats of Formation and Reaction Rates

J. Halpern, H. Okabe **$56,000**
Department of Chemistry

Laser photolysis is an efficient and sudden source of free radicals in the gas phase. Study includes (1) combining laser photolysis with flash absorption spectroscopy and ESR detection to measure the kinetics of polyatomic radicals and triplets to study the reaction kinetics of acetylenic systems; and (2) tunable vacuum ultraviolet light generated in a discharge lamp-monochromator system, or by frequency shifting of an intense laser source to measure the heat of formation of RO radicals (R = CH_3, C_2H_3, and t-C_4H_9). These radicals are important intermediates in combustion and low temperature oxidation of hydrocarbons.

217. Laser Studies of the Dynamics of Atom Molecule Reactions

W.M. Jackson **$56,600**
Department of Chemistry

This project uses tunable dye lasers to measure the reaction rates of CN free radicals as a function of their internal energy. The project is based upon unique photochemical sources of internally excited CN radicals that can be produced from the laser photolysis. Our recent studies have shown that the rate constant for the reaction of CN with NO is enhanced by a factor of 400 by one or more quanta of vibrational excitation in the CN radical. The rate constant for the bimolecular reaction of CN radicals in the $v'' = 0, 1$, and 2 levels with NO are respectively, $1.6 \pm 0.3 \times 10^{-13}$, $5.6 \pm 0.8 \times 10^{-11}$, and $6.2 \pm 1.0 \times 10^{-11}$ all in units of cm^3 $molecule^{-1}$ s^{-1}. Approximately half of the excited radicals are vibrationally quenched by NO, while the other half of the radicals chemically react. The enhancement is thought to be due to a dipole-dipole reaction between the NO and CN radicals leading to CO and N_2. The termolecular rate constant for recombination between the NO and the CN radical using NO and argon as third bodies was also determined. They are $3.2 \pm 0.3 \times 10^{-29}$ cm^6 $molecule^{-1}$ s^{-1} and $6.0 \pm 0.6 \times 10^{-31}$ cm^6 $molecule^{-1}$ s^{-1} using NO and argon respectively as a third body. The termolecular reaction was thought to produce NCNO via a long-lived complex that is stabilized because of the large density of states available to this molecule. The same techniques used for measuring the bimolecular rate constants for reaction of CN radicals have also been used to determine bimolecular rate constants for the reaction of CN with various hydrocarbons and fluorinated ethylenes. Results indicate that the rate constants for the reaction of CN with these compounds is generally very fast. Work is currently in progress to determine the products of the reaction and to clarify the mechanism for the interaction.

University of Illinois
Chicago, Illinois 60680

218. Kinetics of Elementary Atom and Radical Reactions
R.J. Gordon **$75,000**
Department of Chemistry

The objectives of this research are to measure the reaction rates and to study the dynamics of elementary gas phase reactions. One system being studied is O + H_2, D_2, and HD. Flash photolysis with resonance fluorescence detection of oxygen atoms has been used to measure the rate constants of these reactions between 325 and 475 K. The intramolecular branching ratio for O + HD is being determined by using laser-induced fluorescence to measure the relative concentrations of OH and OD products. In a second study the relaxation of highly excited molecules is being investigated by using a CO_2 laser to excite a donor molecule while detecting infrared fluorescence from a receptor molecule. Studies of $SF_6 + N_2O$ and SF_6 + NO yield the VV transfer rate as a function of SF_6 excitation. We have found that the bending mode of N_2O relaxes five times more slowly than the asymmetric stretching mode. In a third study we have investigated the production of electronically excited NH radicals generated by photolyzing HNCO. We have discovered that excited triplet NH is produced in the presence of O_2 or N_2O. The mechanism for this phenomenon, which involves metastable oxygen states, is currently being investigated.

219. Shock Tube Studies of High Temperature Hydrocarbon Pyrolysis Rates
J.H. Kiefer **$75,000**
Department of Chemical Engineering

The purpose of this project is to determine rates and mechanism for fuel hydrocarbon pyrolysis at high temperatures. The measurements are made in the shock tube (providing arbitrary, precise, and externally set temperatures) with two very high resolution laser diagnostic techniques. These two are laser schlieren measurement of density gradient (net endothermic rate) and the new method of excimer laser flash absorption, which provides absorption profiles in the ultraviolet with 3 0.03μs resolution. Previous work has defined much of the pyrolysis kinetics of propane, propene, ethane, ethylene, benzene, and 1,3-butadiene. Recent measurements have given a mechanism and rate for ethylbenzene decomposition and a partial understanding of toluene pyrolysis. Flash absorption measurements at 220 nm have now confirmed the rate and mechanism for 1,3-butadiene dissociation derived from the laser-schlieren data. Flash absorption measurements are now being extended to the study of both ethylbenzene and toluene pyrolysis.

Illinois Institute of Technology
Chicago, Illinois 60616

220. Theoretical Studies of Combustion Dynamics
J.M. Bowman **$66,600**
Department of Chemistry

The objective of this research is to develop and apply approximate but accurate quantum mechanical methods to reactions of interest in gas phase combustion. Such a theory has been developed and applied to the reactions $O(^3P) + H_2$, $O + D_2$, and O + HD using an accurate *ab initio* potential energy surface. Extension of the theory to treat diatom + diatom reactions has been made, and the first application will be to the OH + H_2 reaction. A surface will be obtained from new *ab initio* calculations planned by Dr. Thom Dunning. Work is also underway to calculate the vibrational energies and lifetimes of HCO and HOCO using *ab initio* potential surfaces calculated by Harding. This work is based on a vibrational self-consistent field plus configuration interaction method developed here. The interaction of radiation with long-lived collision complexes is also being investigated. Preliminary calculations indicate that stabilization by stimulated emission may be feasible for small systems using lasers of moderate power.

221. Studies of Combustion Kinetics and Mechanisms
D. Gutman **$120,000**
Department of Chemistry

The purpose of this research is to gain new quantitative knowledge of the kinetics and mechanisms of the reactions of polyatomic free radicals that are important in hydrocarbon combustion processes. The free radicals are generated in a heated tubular reactor by multiple-photon-induced decomposition of suitable precursors by a CO_2 TEA laser or by direct ultraviolet laser photolysis. Ensuing reactions are monitored using a photoionization mass spectrometer capable of recording the time evolution of either reactants or products. Reactions of hydrocarbon free radicals with molecular oxygen are being investigated as a function of pressure and temperature to establish their mechanisms, to measure their rate constants, and to determine important thermochemical parameters. Studies of the $C_2H_5 + O_2$ and $C_3H_7 + O_2$ reactions are revealing important mechanism changes near 700 K that are responsible for important changes in the stable products produced during combustion around this temperature. The equilibria between hydrocarbon free radicals (including CH_3, C_2H_5, C_3H_5, and C_3H_7) with molecular oxygen are being studied between 600 and 700 K to directly measure the enthalpy change of these important combustion reactions. This information is now being used in combustion models that predict flame properties and product distributions.

Johns Hopkins University
Baltimore, Maryland 21218

222. Ionic Aspects of Soot Formation
W.S. Koski **$68,000**
Department of Chemistry

The dynamics and isotope effects were studied for the reaction $CH_3^+(C_2H_2,H_2)C_3H_3^+$. Measurements with CD_3 suggest that the reaction proceeds by addition and insertion mechanisms. The angular distribution of the product ions suggest that a persistent complex ($C_2H_5^+$) was formed with a lifetime longer than 10^{-12} sec. Measurement of the internal energy in $C_3H_3^+$ shows that a large amount of energy can be stored in this ion. In recent years, a controversy has developed over the heat of formation of the vinyl radical. We have measured the threshold for the endothermic reaction $CH_4^+(C_2H_2, C_2H_3)CH_3^+$. This threshold permitted a determination of $\Delta H_f(C_2H_3)$ of 72 ± 2 kcal/mol. This value is consistent with the recommended value for the C-H bond energy in ethylene. The ion ($C_3H_3^+$) is believed to be important in chain build up in combustion processes. We have, therefore, measured the cross sections of a number of reactions of cyclic $C_3H_3^+$ with ten hydrocarbon molecules. No high cross section ion-molecule reactions that would contribute to ion chain build up were observed, suggesting that it is not cyclic $C_3H_3^+$, but more likely the propargylic form of $C_3H_3^+$ that contributes to chain build up.

Kansas State University
Manhattan, Kansas 66506

223. Diffusion Flame Studies of the Chemical and Physical Mechanisms of Soot Formation from Aromatic and Substituted Aromatic Fuels
J.F. Merklin, C.M. Sorensen **$62,000**
Department of Nuclear Engineering

Dilute mixtures of cyclohexane (<1%) in argon were shock heated in a single-pulse shock tube over the temperature range of 950 to 1400 K. We have observed three alkyl substituted cyclohexane compounds (C_8, C_9, and C_{10}), three C_{12} compounds, and a C_{18} compound. Below 1050 K, we do not detect any low molecular weight compounds, so we suggest that the alkyl substituted cyclohexanes come from the scission of the C_{18} hydrocarbon. Above 1050 K, we begin to observe ethylene, 1,3-butadiene, acetylene, and other compounds. The yields of ethylene, 1,3-butadiene are in substantial agreement with literature values. We have measured photon correlation spectra from soot in three CH_4/O_2 flames. We find for moderately sooting flames that the geometric width parameter decreases as height increases. This could be attributed to surface growth. Chemical probing of these flames shows that acetylene is the only species whose concentration decreases with height. The surface growth of the particles could arise from the incorporation of acetylene in the soot particle.

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

224. Aromatics Oxidation and Soot Formation in Flames
J.B. Howard **$90,000**
Department of Chemical Engineering

The objective of this research is to provide basic information on the kinetics and mechanisms of aromatics oxidation and soot formation in flames. The research is based on detailed measurements of profiles of soot particle number concentration, particle size distribution, and stable and radical gas species concentrations through the reaction zone of low-pressure flat premixed flames. Equipment for the project is now being installed. A molecular-beam sampling instrument with on-line mass spectrometry will be used for gas species measurement. Soot particles will be studied by laser scattering and adsorption measurements in the flame and analysis of beam deposits. Net reaction rates calculated from these measurements will be used in screening tests of hypothetical reaction mechanisms. The gas species profiles will be used to test and to extend existing flame chemistry models. The work is expected to lead to an improved understanding of the chemistry of soot formation and aromatics reactions in flames. Calculations using previous data indicate that aromatics in the presence of oxidizing species in flames are consumed more rapidly than in the nonoxidizing conditions of pyrolysis experiments.

225. Depopulation Rates for Combustion-Related Species in Long-Lived ($>100\mu s$) Vibrationally or Electronically Excited Levels
J.L. Kinsey, R.W. Field **$118,000**
Department of Chemistry

In this project, a new technique, stimulated emission pumping, is being used to study individual levels of polyatomic molecules with chemically significant amounts (up to ~3.5 eV) of vibrational excitation. Current effort focuses on the acetylene molecule, HCCH, in its electronic ground state ($X^1\Sigma g$). Individual rotation-vibration levels as much as 28,000 cm^{-1} above the vibrationless level have been studied to obtain information about the transition from regular to ergodic behavior in a molecular system. These studies are being extended to levels near 14,000 cm^{-1} to look for evidence of the vinylidene radical (H_2CC). Parallel investigations are probing triplet levels of acetylene at ~45,000 cm^{-1}, using Zeeman quantum beat spectroscopy and anticrossing spectroscopy. These reveal details of non-adiabatic coupling of triplets to singlet levels of both the $\overline{X}$ and $\overline{A}$ electronic states, and the densities of vibrational levels in this energy range.

University of Michigan
Ann Arbor, Michigan 48109

226. Energy Transfer Properties amd Mechanisms
J.R. Barker **$55,000**
Department of Atmospheric and Oceanic Science **(6 mo.)**

This project studies the mechanisms and properties of energy transfer involving moderate-sized molecules. In part, focus is on resolving current controversies about the temperature-dependence and energy-dependence of $\langle \Delta E \rangle_d$, the average energy transfer step-size in deactivating collisions. Time- and wavelength-resolved infrared fluorescence are used to monitor the level of vibrational energy in excited molecules prepared by pulsed laser excitation. Improvements include (1) tunable ultraviolet laser excitation and tunable excitation in the visible, (2) new calibration methods designed to reduce experimental uncertainties and extend the energy-range of the experiments, and (3) investigation of several molecules that have been studied by time-resolved ultraviolet absorption. Experiments are underway to investigate the mechanisms of energy-transfer. The products of energy transfer are investigated by monitoring their infrared fluorescence, and laser-induced fluorescence is used to assess the importance of vibrational levels produced in the energy-transfer process. Isotopically substituted isomers are used to investigate the effects of dipole moment, symmetry properties, fundamental vibrational frequencies,and so forth. Collisional/reaction master equation calculations indicate whether steady-state is attained in high-temperature systems and whether unimolecular rate theory must be modified to account for the non-steady-state conditions that may occur in hostile environments.

University of Minnesota
Minneapolis, Minnesota 55455

227. *State-to-State Dynamics of Molecular Energy Transfer*
W.R. Gentry, C.F. Giese **$112,000**
Departments of Chemistry and Physics

The project objective is to learn about the transfer and exchange of translational, rotational, and vibrational energy between colliding molecules by measuring state-resolved total and differential cross sections for inelastic molecular collisions as functions of the kinetic energy. The starting point for this project was the construction of a new and unique pulsed molecular beam apparatus that incorporates a laser-induced fluorescence detector. During the first two years, we have investigated energy transfer in the following systems: (1) I_2 + He, H_2, D_2, Ne; (2) $C_6H_5NH_2$ + He; and (3) p-$C_6H_4F_2$ + He. The I_2 results may be summarized qualitatively by considering a simple model in which vibrational excitation is due principally to nearly impulsive collisions in nearly collinear geometries. In the vibrational excitation of aniline, we observed that only the low-frequency out-of-plane modes were excited with significant probability. We have now discovered that in p-difluorobenzene only mode 30, the low-frequency symmetric out-of-plane bend, is excited with significant probability. Results to date point toward one of two possibilities: (1) either the lowest-frequency modes of a polyatomic molecule are unusually active in the energy transfer dynamics or (2) out-of-plane motions are unusually active.

228. *Variational Transition State Theory*
D.G. Truhlar **$75,000**
Department of Chemistry

This research project attempts to develop and implement new methods for calculating rate coefficients for chemical reactions from potential energy surfaces. Emphasis is on gas-phase atom-transfer reactions, an important reaction type in combustion and atmospheric systems, and of fundamental interest. The effect of vibrational excitation of the reactants on chemical reaction rates and kinetic isotope effects are also studied. A very important aspect of our studies is the inclusion of quantal effects in reaction rate calculations, with special emphasis on tunneling (barrier penetration) and on the dependence of vibrational frequencies on the reaction coordinate. We are developing methods to model the potential energy surfaces for simple reactions and to utilize *ab initio* reaction-path Hamiltonians in our calculations. Examples of our applications to reactions important in combustion are $OH + H_2 \rightarrow H_2O + H$, $OH + O \rightarrow H + O_2$, and $O + H_2 \rightarrow OH + H$. We recently have developed new methods for including anharmonicity and a new unified approach to tunneling. We also have begun to model reactions involving tetrahedral carbon.

National Bureau of Standards
Gaithersburg, Maryland 20899

229. *Laser Studies of Chemical Dynamics at the Gas-Solid Interface*
R.R. Cavanagh, D.S. King **$55,000**
Center for Chemical Physics

Internal state distributions characteristic of molecules thermally desorbed from single crystal surfaces in ultrahigh vacuum are used to probe the dynamics of energy transfer at surfaces. Laser excited fluorescence is used to probe NO desorbed from ruthenium(001) and/or platinum(111). Rotational state distributions have been found to be Boltzmann in nature, but the degree of accommodation with the crystal temperature has been found to reflect the dynamics of the final chemical bond-breaking step. The polarization dependence of the LEF signal has been measured. No evidence for rotational alignment has been found in any of these desorption systems. Pronounced non-Boltzmann behavior has been observed in the Doppler profiles of NO desorbed from ruthenium(001). The influence of CO coadsorbed with NO (pre- and post-adsorbed) on the desorption dynamics of NO is being examined. Further measurements on platinum and ruthenium will provide guidelines for testing dynamical models of the energy redistribution associated with chemical reactions at surfaces.

230. *Kinetics Data Base for Combustion Modeling*
W. Tsang, J.T. Herron **$100,000**
Center for Chemical Physics

The aim of this research is to compile, evaluate, and publish information on the rate constants for single-step chemical processes pertinent to the detailed description of hydrocarbon combustion processes. We plan to start with the simplest molecular systems and then to expand into more complicated situations. All possible reactions are considered. Evaluation involves critical examination of experimental data, comparisons with analogous reactions, and expectations from theory. Where data do not exist, estimates are made. Results are presented on individual data sheets so as to permit periodic upgrading. Work on methane and ethane oxidation and pyrolysis has been completed. It should be noted that these reactions form a subset of all combustion processes. Further work will involve continuous updating and expansion into methanol, propane, isobutane, and other higher hydrocarbon systems.

University of New Orleans
New Orleans, Louisiana 70148

231. Identification and Temporal Behavior of Radical Intermediates Formed During the Combustion and Pyrolysis of Gaseous Fuels
R.D. Kern, Jr. **$62,000**
Department of Chemistry

High temperature studies of the gas phase pyrolyses of benzene, toluene, ethylbenzene, butadiene, allene, and acetylene have revealed information pertaining to the mechanisms attendant to aromatic ring rupture and ring formation. The concentration profiles for these decompositions are obtained by analyzing reflected shock zone gas with time-of-flight (TOF) mass spectrometry. By combining the TOF results with data produced by other workers using laser schlieren densitometry and atomic resonance absorption, mechanisms have been constructed that model the experimental profiles successfully. Some important findings include: (1) low concentrations of phenyl radical observed in C_6H_6 pyrolysis; (2) evidence that the primary step in C_7H_8 decay at high temperatures is $C_6H_5 + CH_3$ instead of $C_7H_7 + H$ and the contributions of reverse and secondary reactions; (3) the favored channel is $C_7H_7 + CH_3$ compared to $C_8H_9 + H$ in C_8H_{10} decomposition; (4) the increased amount of C_6H_6 formed during C_3H_4 thermolysis as contrasted to that formed from an equivalent amount of 1,3-C_4H_6; and (5) the role of C_3H_3 in C_6H_6 formation as demonstrated in the decomposition of 1,2-C_4H_6. These facts are most helpful in understanding the problem of soot formation from aromatic fuels.

Princeton University
Princeton, New Jersey 08544

232. Comprehensive Mechanism for Combustion Chemistry: An Experimental and Numerical Study with Emphasis on Applied Sensitivity Analysis
F.L. Dryer **$94,500**
Department of Mechanical and Aerospace Engineering

This project is an integrated effort to determine the reaction mechanisms responsible for oxidation of hydrocarbon and alcohol molecular structures under conditions representative of combustion environments. Such mechanisms are useful to focus on areas where further elementary processes research would be most beneficial, in acting as bench marks against which simplified empirical chemistry results can be compared, and in evaluating the interactions of combustion chemistry within simple one-dimensional, time transient systems with transport. The project necessitates a three-pronged approach: (1) experimental effort for determining pyrolysis and oxidation intermediate and product profiles in a turbulent flow reactor; (2) comprehensive mechanism development and accompanying computer modeling; and (3) application of newly available sensitivity analysis computer tools to extract the maximum information from the first two parts of the research. Efforts are coordinated with the sensitivity analysis research of Rabitz at Princeton, the modeling efforts of Westbrook at Lawrence Livermore National Laboratory, and the fundamental kinetics program of Klemm and Michael at Brookhaven National Laboratory. The experimental aspects of the project are conducted in a flow reactor facility developed at Princeton, which permits chemical kinetic observations at atmospheric pressure, in the temperature range of about 900 to 1200 K, and for reaction times the order of 10 to 500 ms. The modeling aspects of the project are accomplished through use of several recently available computational tools (e.g., HCT, AIM, and CHEMSEN) and other tools and techniques as they become available. Chemical systems of current interest (in order of increasing complexity) are: the CO-H_2-O_2 system, the formaldehyde pyrolysis and oxidation systems, the acetaldehyde pyrolysis and oxidation systems, and the ethanol pyrolyis and oxidation systems.

233. Dynamical Studies of Molecular Systems
H.A. Rabitz **$138,000**
Department of Chemistry

This project has two phases consisting of studies in (1) chemical kinetics and (2) collision dynamics. In the first phase, the research is concerned with the development and application of sensitivity analysis tools for the understanding of complex chemical mechanisms. Both time- and spatially-dependent problems are under study with a special emphasis on combustion phenomena. In the latter case, sensitivity techniques are being developed for probing the role of rate constants, transport coefficients, initial conditions, and boundary conditions on laboratory observables. The second phase of the research in collision dynamics is concerned with understanding the relationship between the structure of potential surfaces and resultant features in observable cross sections and rate constants. Both quantum mechanics and classical dynamics are being studied with emphasis on forward and inverse scattering processes. The ultimate aim of all the research is to understand the interrelationship between a hierarchy of microscopic and macroscopic observables in terms of fundamental potential interactions.

Purdue University
West Lafayette, Indiana 47907

234. Measurement of Radical Species Concentrations and Polycyclic Aromatic Hydrocarbon in Flames by Fluorescence and Absorption via Tunable Dye Laser
N.M. Laurendeau **$87,500**
Department of Mechanical Engineering

New quantitative laser-fluorescence techniques are being developed to measure the concentrations of radical species and polycyclic aromatic hydrocarbons (PAH) in flames. Previously we have: (1) demonstrated laser-saturated fluorescence (LSF) measurements of OH and NH concentrations; (2) performed LSF measurements of OH in sooting flames; (3) developed a calibration procedure for LSF measurements that accounts for nonuniform laser irradiance; (4) developed a technique for quantitatively analyzing PAH mixtures in a vapor cell; and (5) reported the first measurements of atomic hydrogen in flames using two-photon-excited fluorescence. Current research includes: (1) laser-saturated CN and CH measurements; (2) PAH measurements using one- and two-photon excitation; and (3) two-photon measurements of atomic hydrogen and oxygen in flames.

Rensselaer Polytechnic Institute
Troy, New York 12180-3590

235. *Kinetic Measurements on Elementary Fossil Fuel Combustion Reactions Over Wide Temperature Ranges*

A. Fontijn **$80,000**
Department of Chemical and Environmental Engineering

This research project is aimed at providing kinetic data on important isolated elementary hydrocarbon molecule oxidation reactions. Emphasis is placed on measurements in the 1000 to 1800 K range, where accurate data are generally not available, but are needed for development of improved fossil-fuel utilization methods. The high-temperature photochemistry (HTP) adaptation of the flash-photolysis resonance-fluorescence technique is further developed. Use is made of fast electronics, which allows rapid data taking and short residence times, and of on-line microcomputer data smoothing procedures that minimize the number of flashes required. The first objects for study are reactions between oxygen atoms and C_2 hydrocarbons.

Rice University
Houston, Texas 77251

236. *Infrared Absorption Spectroscopy with Color Center Lasers*

R.F. Curl, Jr. **$65,000**
Department of Chemistry

This research project will develop high sensitivity, high resolution methods for detecting and monitoring small free radical species, which are thought to be important intermediates in combustion, by means of infrared absorption spectroscopy using color center laser sources. We have developed two new high sensitivity color center laser spectroscopic methods: (1) magnetic rotation noise suppression and (2) tone-burst modulation, which can be combined with the long pathlengths obtainable with a White cell. In previous work using magnetic rotation, the spectra of C_2H and C_2 were identified in an electrical discharge over polyacetylene. The rotational analysis and fitting of both of these spectra have just been completed. However, for C_2H there remains some uncertainty concerning the correct vibronic assignments. Additional work on this molecule is planned to verify the vibronic assignments by using rotational perturbations to set the vibronic spacings. Current effort is on identifying other radical species present in the discharge over polyacetylene using the recently developed tone-burst modulation technique. We will employ these methods to study the infrared spectra of a variety of free radical species such as HCCN, CH_2OH, CH_3O, and N_2H_3.

237. *Supersonic Metal Cluster Beams*

R.E. Smalley **$78,000**
Department of Chemistry

The pulsed laser-supersonic jet method of preparing beams of bare metal clusters was extended this year to the study of dissociative chemisorption reactions occurring on the surface of the clusters at near room temperature. For the first time it was possible to measure the rate of such reactions as a function of cluster size in the range from one to 40 atoms. In the cases of both D_2 and N_2, the rate of dissociative chemisorption was found to be an extremely sensitive, non-monotonic function of cluster size. Carbon monoxide, on the other hand, was found to exhibit only a slow, smooth increase in reactivity on increasingly large clusters. In parallel work, extensive capabilities are being developed to study mass-selected cold cluster ions. Laser ionization within a special hypersonic nozzle has been shown to produce intense beams of both positive and negative bare cluster ions. These ions have been successfully injected into an ion cyclotron resonance spectrometer where they are trapped for periods of 10 seconds or more, their mass spectrum being observed with resolution exceeding 50,000.

University of Rochester
Rochester, New York 14627

238. *Low Energy Ion-Molecule Reaction Dynamics and Chemiionization Kinetics*

J.M. Farrar **$73,900**
Department of Chemistry

Molecular beam reactive scattering measurements of proton transfer reactions of H_3O^+ and a number of reactions of the ground state carbon cation, including hydride abstraction and C-C bond formation reactions, have been studied with neutral molecules present in hydrocarbon flames with the goal of understanding the dynamics of ionic processes occurring in flames. We have completed studies of proton transfer reactions with CH_3OH and acetone, with special emphasis on the unimolecular decay reactions that the nascent products undergo. Our recent work has focused on the low energy dynamics of C^+ reactions with small molecules. The dynamics are dominated by insertion reactions into O-H and C-H bonds and the subsequent unimolecular decay of the transient insertion complex. C^+ appears to insert into the O-H bond of H_2O, forming a transient $CHOH^+$ intermediate that decays in one rotational period and allows us an estimate of the complex lifetime of 0.1 ps. Reaction of C^+ with methane yields CH_3^+ by hydride abstraction and formation of $C_2H_2^+$ and $C_2H_3^+$ by decay of a transient $C_2H_4^+$ complex. Angular distributions provide information on complex decay geometries and lifetimes. Kinetic energy distributions provide information on intramolecular energy transfer and demonstrate that the production of $C_2H_2^+$ at high collision energies proceeds by sequential ejection of two hydrogen atoms through a transient $C_2H_3^+$ intermediate. Other neutral reagents we have studied include C_2H_2, C_2H_4, C_2H_6, allene, and propyne. Condensation reaction dominates the dynamics of unsaturated hydrocarbons. Work in progress includes reactive dynamics of CH_3^+; we plan to begin O^- studies in the near future.

University of Southern California
Los Angeles, California 90089-1661

239. *Chemistry of the Ethynyl Radical in its $X^2\Sigma^+$ and $A^2\Pi$ States*

C. Wittig **$80,000**
Department of Chemistry

This research concerns the production and subsequent bimolecular chemistry of the ethynyl radical. C_2H is prepared from its low-lying state by the ultraviolet photolysis of acetylenic precursors such as C_2H_2 and C_2HBr and is monitored by laser-induced fluorescence and/or chemiluminescence. Under pulsed molecular beam conditions, it is possible to prepare high C_2H densities and to study the single-collision reactions of these radicals. For example, the reaction of C_2H with O_2 has been shown to yield several product channels, and $CH(X^2\Pi)$ has been observed as a direct product of this bimolecular reaction. This species will be detected in nascent quantum state under single collision conditions in order to further clarify the reaction mechanism(s). By photolyzing the C_2H precursors at different distances from the interaction regions, we will alter the participation of the $A^2\Pi$state and will establish the role of this low-lying ($\sim$0.5 eV) state.

SRI International
Menlo Park, California 94025

240. *Combustion Research Program: Flame Studies, Laser Diagnostics, and Chemical Kinetics*

D.R. Crosley **$117,000**
Molecular Physics Laboratory

This research project involves a combination of laser-induced fluorescence (LIF) and chemical kinetics measurements to investigate the chemistry of hydrocarbon and ammonia combustion processes. The research comprises several related parts: (1) LIF probing of flat flames; (2) the development of an LIF spectroscopic and collisional data base; (3) computer modeling of combustion chemical networks; (4) development and application of rate constant estimation methods; and (5) a laser pyrolysis (LP)/LIF experiment. In LP/LIF, a mixture containing SF_6 is rapidly heated by a pulsed CO_2 laser, with time-resolved LIF measurements of radical concentrations, temperature, and excited level decay times. Measurements of the $OH + C_2H_2$ rate constant show an abstraction (addition) mechanism dominating above (below) 1000 K, agreeing with theoretical calculations of the combined pressure/temperature dependence of the addition channel. LP/LIF reaction rate measurements on $OH + CH_4$, C_3H_8, C_3H_6, and NH_3 have also been made. Calculations on the $H + N_2O$ reaction and $CH_3 + CH_3$ recombination show bound intermediates and very different rate constant expressions from those currently used. The LIF spectroscopy of the $A^3\Pi_i - X^3\Sigma^-$ system of NH in a flow system has yielded lifetimes and transition probabilities. Quenching of electronically excited OH by NH_3 and NH by NH_3 and CO has been studied at high temperature on LP/LIF. The LIF flame spectra of NH_2 in NH_3-O_2-N_2O flames is being cataloged.

Stanford University
Stanford, California 94305

241. *Combustion Gas Spectroscopy Using Tunable Lasers*

R.K. Hanson **$74,000**
Department of Mechanical Engineering

Objectives of this research are: (1) the measurement of fundamental spectroscopic parameters (absorption coefficients, oscillator strengths, fluorescence quench rates, and collision widths) for critical combustion species, particularly pollutants and radicals; and (2) the development of tunable laser absorption and fluorescence techniques for species measurements in studies of chemical kinetics. Laser sources include a tunable CW infrared diode laser, a tunable CW ring dye laser, and a discretely tunable CO laser. Species studied include HCN, CO, OH, NH, NCO, and NO. Measurements are made over a range of conditions in a controlled-temperature absorption cell, in the post-flame region of a flat flame burner, and in a shock tube.

242. *The Kinetics of Cyano Compounds at High Temperature*

R.K. Hanson, C.T. Bowman **$73,500**
Department of Mechanical Engineering

The objective of this research project is to obtain high-temperature kinetic data for reactions involving HCN, CN, and NCO. These data are relevant to the formulation of reaction mechanisms for pollutant formation in flames. Reactions of interest include: (1) the reactions of HCN with OH; (2) the reaction of CN with OH; and (3) the reaction of NCO with OH. A conventional shock tube technique is combined with spectroscopic diagnostics to study the mechanisms and rates of candidate reactions. Experimental data are compared with results obtained from detailed kinetic models.

State University of New York/Buffalo
Amherst, New York 14260

243. *Multiphoton Interactions in Molecules with Picosecond Laser Pulses*

H.S. Kwok **$67,000**
Department of Electrical and Computer Engineering

High-power picosecond laser pulses are employed in this project to study the multiphoton absorption and dissociation behavior of simple polyatomic molecules. Tunable 20 to 200 ps CO_2 and dye laser pulses are used individually or in a pump-probe arrangement to measure the excitation characteristics of vibrationally hot molecules. Intramolecular and intermolecular energy transfer rates are studied in the collisonal and collisionless regimes. Information on the vibrationally hot molecules in the quasicontinuum is of vital importance in the understanding of gas phase reaction dynamics. During the past year, it was found that the multiphoton absorption spectra in SF_6 and C_2F_5Cl were inhomogeneously broadened. Intramolecular energy transfer did not seem to contribute to any line broadening at all, contrary to some prevalent belief. It was also discovered that the absorption cross section increased significantly as the CO_2 laser pulse duration was decreased. These observations were consistent with a coherent N-level Bloch equation description of the MPE process. Picosecond ultraviolet-infrared double resonance experiments are planned for the coming year.

State University of New York/Stony Brook
Stony Brook, New York 11794

244. *Multiphoton Ionization Spectroscopy and Photochemistry of Transient Species*

P.M. Johnson **$70,000**
Department of Chemistry

This project is primarily concerned with the development of new methods of acquiring the multiphoton spectra of transient species such as triplet metastables and radicals. These species are generated in ways related to combustion processes so that insight may also be gained into the production mechanisms. In one method, radicals and triplets are generated by a pulsed electric discharge at the orifice of a pulsed supersonic valve, providing cooling in the expansion and a rapid transition into a collisionless condition. This technique has proven to be a bountiful source of triplet and radical species whose multiphoton spectra have never been explored. It should also be possible to create discharge-initiated reactions between two species in the expansion. Reaction intermediates will be rapidly isolated by the expansion and can be studied by multiphoton ionization mass spectrometry. To date, we have successfully studied the triplet states of argon, carbon monoxide, and nitrogen as well as the radical CCl. By using this technique, we have been able to precisely determine the energy of the lowest triplet state of benzene.

University of Utah
Salt Lake City, Utah 84112-1183

245. Study of Combustion and Flame Processes Initiated by Infrared Laser-Induced Absorption
W.A. Guillory **$80,000**
Department of Chemistry **(24 mo.)**

The phenomenon of infrared multiple-photon absorption (IR MPA), subsequently leading to excited and ground state dissociation products, simulates nonequilibrium processes occurring in flames and other combustion systems. Using visible and ultraviolet laser-induced fluorescence diagnostics as probes of the reaction zone, highly sensitive time- and wavelength-resolved spectroscopy allow detailed determination of the mechanisms and energetics of a given system. The reactions of vibrationally excited ground electronic state CH and OH (produced by IR MPA) with O_2, N_2, NO, and aliphatic and aromatic hydrocarbons are being studied. Also being studied is the efficiency and means of production, via IR MPD, of CH, NH_2, and OH from various precursors. Current studies involve the state-selective reactions of $CH(V'' = 0, 1)$ and $NH_2(V_2'' = 0, 1)$ and the vibrational relaxation of $NH_2(V_2'' = 1)$.

University of Wisconsin
Madison, Wisconsin 53706

246. Unimolecular Reaction Dynamics
F.F. Crim **$69,900**
Department of Chemistry

This project is an experimental study of the unimolecular decay dynamics of internal energy selected molecules using direct production of highly vibrationally excited molecules by dye laser excitation of overtone vibrations in conjunction with time-resolved spectroscopic detection. Excitation of an overtone vibration prepares a molecule with a large excess of energy initially isolated in a small subset of the available vibrational modes. Time-resolved spectroscopic detection provides a direct measure of the unimolecular reaction rate constant and, in favorable cases, the energy partitioning in the products. Work includes excitation of CH and OH overtone vibrations and product detection using both visible chemiluminescence and laser induced fluorescence. Chemiluminescence techniques have now provided the first direct measure of the unimolecular decay rate of a selectively excited, ground electronic state molecule cooled in a supersonic expansion. In these measurements, a pulsed dye laser excites a cyclic peroxide (tetramethyldioxetane) in a molecular beam, and time-resolved detection of the product chemiluminescence provides the unimolecular decay rate. Laser-induced fluorescence experiments that detect the OH product of the vibrational overtone-initiated unimolecular decay of hydrogen peroxide (HOOH) have given a view of the partitioning of the excess energy among product quantum states and, through careful analysis of the vibrational overtone excitation spectra, have uncovered new details about highly vibrationally excited molecules. These detailed studies critically test statistical theories of unimolecular reactions and provide data on the dynamics of isolated molecules potentially useful in understanding atmospheric chemistry, combustion processes, and laser-induced reactions.

Wright State University
Dayton, Ohio 45435

247. Direct Determination of Atom and Radical Concentrations in Thermal Reactions of Hydrocarbons and Other Gases
G.B. Skinner **$61,400**
Department of Chemistry

The general objective of this research is to study the kinetics of the atom and free radical reactions that are important in combustion by following the appearance and disappearance of these combustion intermediates. Hydrogen, deuterium, and oxygen atoms are currently being measured in shock tube experiments using resonance absorption spectroscopy in the vacuum ultraviolet. The shock tube can operate over a range of 0.4 to 3 atm, so the dependence of reaction rates on total pressure can be studied. Our earlier measurements were in the 2 to 3 atm range, while recently we have studied several reactions near 0.4 atm. These include pyrolysis of benzene-d_6, toluene-d_8, chlorobenzene and bromobenzene (in order to study dissociation of the phenyl radical), vinyl bromide, partially deuterated propenes, and the reaction of hydrogen atoms with acetylene-d_2. These are all key reactions in combustion chemistry.

Yale University
New Haven, Connecticut 06520

248. Simultaneous Multipoint Measurements of Density Gradients and Temperature in a Flame
M.B. Long, R.K. Chang, B.T. Chu **$68,000**
Section of Applied Physics and Department of Mechanical Engineering

Our research focuses on the development and application of non-intrusive optical techniques for making two-dimensional measurements in turbulent reacting flows. A central theme has been to take advantage of developments in computer-controlled low-light-level imaging systems to provide data at a large number of spatially resolved points (typically 10,000). Recent efforts have led to progress toward developing techniques that will measure the spatial characteristics of turbulent flows and follow their temporal evolution. In addition, progress has been made in recording a significant number of frames (about 500) at a framing rate high enough to follow the evolution of structures in turbulent flows. Another significant advance is the development of an imaging technique that can provide both temperature and species information in two dimensions in a single laser shot. Two cameras are used, with one detecting the Rayleigh scattered light from which the temperature is determined and the other monitoring the Raman scattering, which gives information on species concentration. This technique has been applied to both premixed and non-premixed flames.

Atomic Physics

Atlanta University
Atlanta, Georgia 30314

249. Theoretical Investigation of Electron-Ion Interaction

A.Z. Msezane **$54,000**
Department of Physics

The purpose of this project is to identify and calculate dominant physical mechanisms underlying the processes of electron impact excitation and ionization of ions using the close-coupling approximation. Both total and differential cross sections are calculated and compared with measurements. In particular, detailed numerical studies are carried out to investigate the extent of contribution of the physical processes of inner-shell excitation-autoionization and inner-shell resonant excitation-double autoionization to the total ionization cross section of Ti^{+3}, important in CTR plasmas. Total and differential cross sections for electron impact excitation of cadmium(II), important in the He–Cd(II) hollow-cathode laser, are compared with measurements from energy loss spectrum and line emission data. An accurate configuration interaction wave function of the target is used to give the energy splittings between the ground state and the various excited states of interest very close to the observed values and the same values for the oscillator strengths in the length and velocity formulations.

University of Chicago
Chicago, Illinois 60637

250. Basic Studies of Atomic Dynamics

U. Fano **$70,000**
James Franck Institute

This project aims at describing and predicting the correlations and energy transfers among the variables of atomic and molecular systems. It has stressed that key processes are often localized on top of potential barriers rather than in potential valleys. A major step has been made this year by showing how to graft the resonant states analytically onto the more familiar states that propagate adiabatically along potential valleys. Implementation of this procedure should permit us to calculate for the first time the excitation of Rydberg levels in a magnetic field and the partition of energy between two excited electrons in integrated fashion. A new very efficient quantitative and transparent analysis of spectral perturbations has been introduced that can now be applied throughout the periodic system.

College of William and Mary
Williamsburg, Virginia 23185

251. Collisional Detachment of Negative Ions

R.L. Champion, L.D. Doverspike **$84,000**
Department of Physics

The fundamental goals of these experimental studies are (1) to determine various cross sections and (2) to develop a general understanding of the collisional dynamics for systems that involve negative ions. The energy range of the experiments is from a few electron volts up to 500 eV. The experiments involve measurements of absolute total cross sections and doubly differential cross sections. The processes under investigation include collisional detachment, charge transfer, dissociative charge transfer, reactive scattering, and inelastic scattering. Emphasis is placed on elucidating the role of competing product channels in negative ion-molecule collisions and on delineating the various collisional processes that may occur in collisions of negative ions with molecular targets. Systems under investigation include hydrogen, deuterium, and alkali negative ions in collisions with hydrogen, deuterium, alkali atoms, O_2, N_2, CO, CO_2, and CH_4. The experimental results are coupled with theoretical models to provide a basis for understanding the role of negative ions in various environments.

University of Colorado
Boulder, Colorado 80309

252. Spectroscopic Diagnostics of Electron-Atom Collisions

A.C. Gallagher **$82,000**
Joint Institute for Laboratory Astrophysics

An experiment has been initiated to measure cross sections for electron excitation of metal atoms. The experiment is designed to yield differential cross sections for spin and angular momentum changes as a function of electron scattering angle. The experimental plan utilizes laser excitation to high levels of atoms first excited by electron collision, and detection of the resulting fluorescence from a beam of atoms in a magnetic field. Each sublevel excited by the electrons is spectrally resolved, and partial cross sections for exciting each state are obtained from the optical excitation spectrum. The atomic recoil energy distribution resulting from the electron excitation is obtained from the Doppler shift of the absorption line from each substate.

253. Near-Resonant Absorption by Atoms in Intense Fluctuating Fields

S.J. Smith **$94,000**
Joint Institute for Laboratory Astrophysics

This research is directed to the measurement of photon absorption by atoms immersed in very intense laser radiation fields near an atomic resonance. A primary objective is the accurate comparison of atomic absorption in a strong monochromatic field with the absorption in a strong field on which statistically well-characterized frequency fluctuations are superimposed. A hybrid system of electro-optic and acousto-optic modulators is used to impose laser bandwidths up to 30 MHz and bandshapes out to 1 GHz from line center on a single-mode laser beam. Lineshapes ranging from Gaussian to Lorentzian are synthesized by controlling the time scale of the fluctuations. The role of fluctuations in nonlinear atomic absorption was measured in the two-photon 3^2S–5^2S transition in sodium, in a Doppler-free configuration. Measurements are in progress on the saturated $3S_{1/2}(F = 2, M_F = 2) \rightarrow 3P_{3/2}(F = 3, M_F = 3)$ transition in a highly collimated atomic sodium beam using an optical double-resonance technique to study broadening, shifting, and splitting of the upper level as a function of laser intensity, detuning, and fluctuation parameters (linewidth and lineshape).

Cornell University
Ithaca, New York 14853

254. *Experimental Study of Interactions of Highly Charged Ions with Atoms at keV Energies*

V.O. Kostroun **$185,000**
Nuclear Science and Engineering Program

This project involves the development of electron-beam ion sources capable of producing low-energy very highly charged ions (up to and including bare nuclei) and the experimental study of interactions of such ions with atoms, ions, and electrons. The recent goal has been to finish construction (begun in August 1983) of a superconducting solenoid cryogenic electron-beam ion source designed to produce initially bare argon ions at a kinetic energy of $\leq$ 2.25 keV/nucleon. Longer range goals are to gradually upgrade the source to handle a 25 kV, 1 A electron beam that could be used to produce helium-like xenon. By March 1985 most of the components of the source were constructed and tested. The source should be ready for final tests by early June 1985 and will be used to investigate low-energy charge transfer to bare, hydrogen-, and helium-like argon. Total and partial cross sections for populating specific states of the projectile as a function of its energy in collisions with molecular hydrogen and helium will be determined. Specific states of the projectile will be selected by high resolution energy-gain spectroscopy.

University of Georgia
Athens, Georgia 30605

255. *Quantum Mechanical Studies of Heavy-Ion Scattering Processes*

T.G. Heil **$67,000**
Department of Physics and Astronomy **(15 mo.)**

This research project concentrates on low to intermediate energy processes where a quantum mechanical description is most appropriate. Several heavy-ion processes involving important constituent reactions that take place in terrestrial and astrophysical plasmas are being studied in detail. Angular distributions are being calculated and interpreted for charge transfer reactions and other low-energy heavy-ion processes. These may prove to be a sensitive probe of the dynamics of low-energy many-body collisions. Charge transfer processes between hydrogen atoms and multiply charged ions by both radiative and nonradiative mechanisms are also being studied. The charge transfer reactions [$C^{+2} + H \rightarrow C^{+} + H^{+} + h\nu$] and [$Al^{+3} + H \rightarrow Al^{+2} + H^{+}$] are being examined in detail.

Harvard University
Cambridge, Massachusetts 02138

256. *Theoretical Studies of Highly Ionized Species*

A. Dalgarno **$134,000**
Harvard-Smithsonian Center For Astrophysics

Studies are made of collisions of multiply-charged ions with neutral gas affecting the ionization structure, thermal balance, radiation losses, and ion transport in plasmas containing a neutral component. Because the products of the collisions radiate, they can be detected and thereby provide unique diagnostic probes of the environment. We have extended our calculations of the efficiencies of the processes so that their accuracy can be assessed by comparison with experimental data. We have investigated the role of proton impact-induced transitions on the fine-structure populations of hydrogenic ions. A multi-channel diabatic theory of collisions has been applied to photodissociation processes.

Jackson State University
Jackson, Mississippi 39217

257. *Spectroscopy of Trapped Molecular Ions*

B. Hale, J. Perkins **$55,000**
Department of Chemistry **(18 mo.)**

The aim of this research is to obtain spectroscopic measurements of molecular ions (e.g., CO^{+}, CN^{+}, NH^{+}, and NH_2^{+}) confined in an R-F quadrupole trap. The ions will be produced by electron impact and dissociative ionization, and stored in the R-F trap for spectroscopic measurements. The ion trap also allows mass selection during this waiting period to further simplify the spectra. Laser-induced fluorescence will be used to obtain a rotationally resolved spectrum of the trapped ions. The probe laser will be scanned in wavelength and the total fluorescence observed.

University of Kansas
Lawrence, Kansas 66045

258. *Theoretical Studies of Many-Body Processes in Atomic and Molecular Physics*

S.I. Chu **$68,000**
Department of Chemistry

The fundamental goals of this project are to develop new theoretical formalisms and practical numerical methods for probing intense field atomic and molecular multiphoton processes. Several new developments in semiclassical Floquet theory and quasienergy methods are currently under investigation: (1) extension of conventional one-mode Floquet theory to the many-mode theory, allowing exact treatment of multiphoton excitation processes in the presence of more than one laser field; (2) non-adiabatic theory for studying resonant infrared multiphoton absorption spectroscopy; (3) most probable path approach for selecting the most important multiphoton excitation path, using artificial intelligence algorithms, allowing the study of multiphoton dynamics to very high order; and (4) coupled dressed-quasimolecular-states approach for the study of laser-assisted charge-transfer reactions in slow ion-atom collisions.

Kansas State University
Manhattan, Kansas 66506

259. *Atomic Physics of Strongly Correlated Systems*

C.D. Lin **$94,737**
Department of Physics

This project is directed toward the understanding of correlations and classification of two-electron atoms in hyperspherical coordinates and the development of practical computer codes for calculating inelastic cross sections in ion-atom collisions. The molecule-like normal modes of doubly excited states are being studied within the hyperspherical methods. Two-center atomic orbital expansion method and a unified AO-MO matching procedure are being developed to study collisions at low energies for excitation and charge transfer processes in multi-electron ion-atom collision systems.

260. *Atomic Physics with Highly Charged Ions*
P. Richard **$605,000**
Department of Physics

High velocity, highly charged ions produced by the 6 MV KSU tandem Van de Graaff as well as higher energy beams from larger facilities off-site are used to study charge transfer, ionization, and excitation in ion-atom collisions. Electron capture by highly-charged ions is studied at very low projectile velocities. Investigation of interference effects in K-K transfer were extended to heavier systems (Ge^{+31} on krypton) using UNILAC beams at GSI. Measurements of the 1s Lamb shift in chlorine were continued and a measurement in krypton completed. The impact parameter dependence of multiple ionization in low-energy collisions was investigated at intermediate scaled velocities, while measurements of total cross sections for multiple ionization by relativistic uranium ions were initiated at the Berkeley BEVALAC. Translational energy spectroscopy for very-low-energy electron capture by neon and argon projectiles from atomic and molecular targets has been performed, and angular distributions for capture by similar projectiles from helium measured. Electron spectroscopy on very-low-energy ions bearing K-vacancies has been initiated. Theoretical work on high velocity electron capture has eliminated many previously employed approximations. Calculations of theoretical lifetimes, transition energies, and branching ratios have been carried out for two-electron ions for configurations involving both electrons above the K-shell.

Louisiana State University
Baton Rouge, Louisiana 70803-4001

261. *Electron Collisions with Positive Ions*
R.J.W. Henry **$60,000**
Department of Physics and Astronomy

The fundamental goal of this project is to delineate the important physical processes governing electron impact excitation processes for impurity ions in high temperature plasmas of interest in thermonuclear reactors. The energy range considered is from the threshold to approximately four times the ionization energy. Calculations are based on a close-coupling expansion, which includes the important physical effects of electron exchange and resonances. Calculations are made for inner-shell excitation-autoionization contributions to total ionization for Be^+ and B^{+2}. These supplement our previous calculations on C^{+3}, N^{+4}, and O^{+5}. For all cases except Be^+, the close coupling theory is in agreement with the deduced experimental excitation cross sections. Differential electron scattering cross sections for inelastic excitation of Mg^+ are calculated at energies between 15 and 100 eV. Agreement of theory with experiment at 35 and 50 eV is very good over the measured angular range of 4 to 16°.

University of Louisville
Louisville, Kentucky 40292

262. *Spectroscopic Studies of Hydrogen Atom and Molecule Collisions*
J. Kielkopf **$64,872**
Department of Physics

This is an experimental laser-spectroscopic study of hydrogen atom and molecule interactions and the energetics and dynamics of molecular hydrogen collisions. The purpose of the study is to probe collisional energy transfer in the hydrogen molecule (and its isotopic variants), atom-molecule interactions, and the interactions of the hydrogen atom with noble gas atoms. Radiative collisions are analyzed, taking into account both binary and multi-perturber encounters, to find descriptions of the detailed processes that occur during collision. For the hydrogen atom, since its interaction with other atoms can often be calculated in detail, studies of the effects of the deviation from classical trajectories, interference due to the quantal nature of the collisions, collisional narrowing, and non-adiabatic transitions are possible. The project goal is to elucidate the basic collisional processes involving the hydrogen atom and the hydrogen molecule and the effects of neutral atom and molecule collisions on atomic spectral lines.

University of Missouri/St. Louis
St. Louis, Missouri 63121

263. *Low Energy Ion-Neutral Collisions*
J.J. Leventhal **$73,500**
Department of Physics

This experimental project is designed to investigate energy transfer and energy conversion in atomic and molecular interactions. Current emphasis is on the study of interactions involving atoms in specific (laser-excited) electronic states and the study of ion-atom energy transfer in which energy disposal is affected by emission of visible and/or vacuum ultraviolet radiation. By using both spectral analysis of the radiation emitted by the reaction products and mass analysis of ionic products, nearly complete characterization of the interactions can be achieved. Of particular interest at this time is examination of the microscopic processes that collectively lead to macroscopic effects, such as plasma formation. The possibility of modifying these macroscopic effects using laser-induced chemistry is also being investigated.

National Bureau of Standards
Boulder, Colorado 80303

264. *Atomic and Molecular Collision Processes*
D.W. Norcross **$96,000**
Quantum Physics Division

This project studies the physics of low-energy collisions of electrons with atoms, ions, and molecules, with an emphasis on detailed computational studies of fundamental processes involved in laser and fusion plasmas. Recent progress in the theory of electron-molecule collisions includes: (1) general code development to include nuclear dynamics and exchange effects more rigorously and to obtain bound states of molecular negative ions; (2) extension of earlier work on vibrational excitation of HCl; and (3) new calculations of vibrationally elastic scattering by HF, HCN, and CO. Our latest results for vibrational excitation of HCl are in excellent agreement with measurements except at very near threshold, where complete treatment of nuclear dynamics is expected to remove remaining discrepancies. The facility to obtain energies of molecular negative ions will complement our results for resonance energies in HF and HCl, and in the isoelectronic molecules N_2, HCN, and CO. In the area of electron collisions with atomic ions, we have made some progress in resolving a serious discrepancy between theory and measurements for excitation of Be^+. It now appears that we have a null result, leading to the conclusion that calibration techniques used in the measurements are seriously flawed.

National Bureau of Standards
Gaithersburg, Maryland 20899

265. Electron-Atom Collision Studies Using Optically State Selected Beams
R.J. Celotta, M.H. Kelley **$65,000**
Radiation Physics Division

Coherence and correlation techniques in atomic collision experiments are being used to improve our understanding of the interactions important in the atomic collision process. Production and detection of spin polarization in free electron beams and laser optical pumping methods for the production of polarized atomic beams have been used to study electron-atom collisions using quantum state selected beams. Such studies provide the maximum allowable information about the interaction, and require an experimental arrangement only slightly more complicated than a conventional crossed beam scattering apparatus. A scattering apparatus using optically selected beams capable of very general studies of collisions between spin polarized electrons and spin polarized atoms has been constructed. This facility will be used to comprehensively study the role played by electron spin in electron-atom interactions. In particular, for alkali atoms, the exchange interaction and the spin-orbit interaction in elastic, inelastic, and superelastic collisions will be examined. Studies of the spin dependence in superelastic scattering will be the focus of current efforts.

University of Nebraska
Lincoln, Nebraska 68588-0111

266. Hyperspherical Coordinate Theory of Two-Electron Processes
J.H. Macek, A.F. Starace **$68,000**
Department of Physics and Astronomy

In this project electron correlations are studied in two-electron atoms using theoretical methods employing hyperspherical coordinates. The doubly differential cross section for detachment of H^- by impact with helium is studied using adiabatic hyperspherical coordinate initial and final state wavefunctions to compute the H^- form factors. The detached electron's angular distribution is highly sensitive to electron correlations. A pseudo-state method is developed to correct the gross inaccuracies of adiabatic hyperspherical wavefunctions at large radial distances. This procedure yields significantly improved ^1S elastic phase shifts for electron scattering on atomic hydrogen. The Fock series expansion for two-electron wavefunctions has been successfully implemented numerically. When matched to single channel adiabatic functions for some radius R_0, the Fock wavefunctions for helium and H^- differ little (for $0 < R < R_0$) from the adiabatic wavefunctions, at least for the lowest adiabatic channels. This confirms other recent theoretical results. The R-matrix for systems of coupled differential equations containing first derivative coupling matrix elements is found to be asymmetric. An alternative matrix (equal to the sum of the inverse R-matrix and the first derivative coupling matrix) is found to be symmetric. The Wannier threshold energy dependence of cross sections and angular distributions is derived quantum mechanically for the Coulomb breakup of three-particle systems with arbitrary angular momentum.

University of New Mexico
Albuquerque, New Mexico 87131

267. Atomic Physics with Relativistic Beams
H.C. Bryant **$85,000**
Department of Physics and Astronomy

Exploitation of the relativistic kinematics of an 800 MeV H^- beam at the Clinton P. Anderson Meson Physics Facility (LAMPF) at Los Alamos allows the observation, with very little background, of the one- and two-electron continua and embedded resonant structures. The H^- system is being studied using Doppler-tuned laser probes and motional electric fields, which have so far ranged up to 3.5 MV/cm, far in excess of those possible using more conventional laboratory techniques. The behavior of the H^- system as a function of both excitation energy and applied field is being carefully mapped out. Energy scale calibration is provided by excitation, with single photon absorption, of the Lyman series in an H^0 beam, derived from the H^- beam by photodetachment. Studies of the ^1P resonant structures in H^- and the two threshold regions are exceptionally challenging to atomic physics theory, and more detailed measurements in these regions are planned. Recently we have applied our technique to elucidate the response of the H^0 atom to strong electric field, in particular, the line shapes of the Stark manifolds for low-lying ($n = 4$) states, and the Luc-Koenig oscillations in the continuum.

New York University
New York, New York 10003

268. Energy-Related Atomic and Molecular Structures and Scattering Studies
B. Bederson **$88,000**
Department of Physics

Atomic, molecular, and cluster interactions with static and dynamic fields and with low-energy electrons are studied. This work seeks to elucidate the role played by long-range forces in atomic and molecular physics and in the structure of small polar-molecular clusters. We have recently completed a series of measurements of the electric dipole polarizabilities of all twenty alkali-halide dimers, and have developed a simple combined spring and ionic model to derive values that are in generally good agreement with our measurements. Very accurate determinations of ground-state polarizabilities of several heavy column IIIa elements (indium and thallium) have been made. Measurements of total effective cross sections for scattering of low-energy electrons by four alkali-halide monomers have been performed. Differential cross section studies are now in progress. Extension of both polarizability and scattering measurements to clusters will soon be initiated.

University of North Carolina
Chapel Hill, North Carolina 27514

269. *Experimental Studies of Atomic Inner Shell Ionization Phenomena*
S.M. Shafroth **$73,000**
Department of Physics and Astronomy

This project is designed to study inner-shell vacancy production in ion-atom collisions and subsequent decay via x-rays or Auger electrons. Dielectronic recombination cross section information is extracted by means of coincidence measurements between projectile K-X-rays and fast moving projectile ions that have captured an electron while passing through a target gas at the appropriate velocity (resonant transfer and excitation). A background process that interferes with these measurements has been clarified (nonresonant transfer and excitation). Additional processes such as projectile K-electron excitation followed by K-X-ray emission and simultaneous electron loss are being studied. Target K-X-ray production, projectile ion-electron capture and loss, and coincidences with projectile ions that have gained or lost one or two electrons are studied. A high efficiency electron spectrometer, capable of resolving closely spaced Auger electron lines emitted from fast moving projectiles, has been built. A redesigned target chamber and beamline are under construction at the Triangle Universities Nuclear Laboratory, where an FN tandem (terminal voltages greater than eight million volts) Van de Graaff produces fast ion beams. This research is relevant to fusion power, particle beams, x-ray lasers, and fundamental processes occurring in the solar corona. It leads to deeper understanding of fast ion-atom interactions.

Rice University
Houston, Texas 77005

270. *Theoretical Atomic and Molecular Sciences*
N.F. Lane **$110,000**
Department of Physics

Theoretical quantum-mechanical and semi-classical methods are used to investigate various atomic and molecular collision phenomena of fundamental interest and, in some cases, that are relevant to dense, high-temperature plasmas and other energy research environments. Current research projects include: (1) development and application of L^2 methods to Penning ionization of alkali atoms (and eventually clusters) in slow collisions with metastable helium atoms; (2) inelastic ion-ion and electron-ion scattering in dense, high-temperature fusion plasmas; (3) semi-classical studies of excitation and excitation-transfer in slow collisions between highly-excited atoms and molecules; (4) ro-vibrational excitation in electron-molecule collisions; and (5) charge-transfer in ion-atom and ion-molecule collisions.

University of Rochester
Rochester, New York 14627

271. *Nonlinear Optics with Broad-Band Lasers*
M.G. Raymer **$90,000**
Institute of Optics

Experiments are being carried out to understand the statistical properties of broad-band laser radiation, and the effects of using such radiation in several areas of nonlinear optics. Intensity fluctuations and mode correlations are being studied in both cw and pulsed broad-band dye lasers via intensity autocorrelation and spectral measurements. Such broadband lasers are being used to pump stimulated Raman amplification and coherent anti-Stokes Raman scattering in hydrogen gas. Intensity and field cross-correlations that develop between pump and probe laser beams in these processes are being observed, using an intensity cross-correlator and a nonlinear interferometer based on the interference of beams produced at the sum-frequency of the two beams of interest.

Smithsonian Astrophysical Observatory
Cambridge, Massachusetts 02138

272. *Measurements of Ionization Balance Parameters in Atomic Ions*
J.L. Kohl **$103,000**
Division of Atomic and Molecular Physics

An inclined electron-ion beams experiment has been developed to measure absolute dielectronic recombination (DR) cross sections as a function of the applied electric field. The DR event rate is measured by detecting two products of DR in delayed coincidence: (1) the stabilizing photon and (2) the recombined ion. This technique discards events from charge transfer that occur 10^7 times more frequently than DR. Recent results for the near threshold cross section for electron impact excitation of C^{+3}(2s-2p) have helped to establish the absolute scales for the DR cross section and the electron energy. An initial attempt to measure C^{+3} DR in a small external field (<1.1 V/cm) provided an upper limit on the cross section. Several improvements include modification of the beam transport system to increase ion currents, the addition of a parallel plate analyzer upstream of the beams' intersection region to remove background ions, a new vacuum pump, and an adjustable magnetic field along the electron beam, which provides increased electron flux and a known electric field in the ion rest frame. These improvements should lead to accurate DR cross sections in C^{+3} and other systems and a direct experimental test of DR enhancement by field mixing.

St. John Fisher College
Rochester, New York 14618

273. *Multilevel Relaxation Phenomena and Population Trappings*
F.T. Hioe **$65,000**
Department of Physics

In this research project: (1) the newly discovered theory of multilevel adiabatic following will be extended to the study of selective multistep photoionization; (2) experiments will be suggested for observing multiphoton echoes and for understanding multiphoton relaxations; (3) a more complete theory of Landau-Zener effect at avoided crossings for multilevel systems will be formulated in relation to the optimum rate for accomplishing population inversion; and (4) multiple pulse propagation and the possibility of observing self-steepening or optical shocks will be explored.

University of Tennessee
Knoxville, Tennessee 37996-1320

274. Production and Destruction of Metastable Negative Ions

D.J. Pegg **$92,000**
Department of Physics

This project will investigate the production and destruction of metastable negative ions. The studies have been started with Ca^- which is believed, from theoretical results, to exist in the $(4s4p^2)^4P$ state. These ions have been successfully produced from an energetic beam of Ca^+ ions by double electron capture processes in a lithium vapor target. The yields of Ca^- ions have been measured in a projectile energy range from 20 to 100 keV. We are attempting to detect the discrete but low energy electrons that are a signature of the break-up in flight of the unstable Ca^- by autodetachment. Energy analysis of such electrons would permit us to determine the binding energy of the metastable state responsible for the existence of Ca^-. In similar measurements on another metastable negative ion of the alkaline earths (Be^-) these autodetachment electrons have been observed and collected. Energy analysis of the electrons, once corrected for kinematical effects, has allowed us to determine that the Be^- ion exists in the metastable $(2s2p^2)^4P$ state, which has been found to have a binding energy of 190 meV with respect to the $(2s2p)^3P$ state of the beryllium atom.

University of Texas
Austin, Texas 78712

275. Kinetic Studies Following State Selective Laser Excitation

J.W. Keto **$80,000**
Department of Physics

Electronic energy transfer from xenon atoms and excimers is studied following selective excitation by multiphoton laser excitation. Reactions at higher pressures where intermolecular processes are observed are being emphasized. Initial experiments are studying radiative lifetimes and quenching of $5p^56p$ xenon atoms in collisions with xenon and other rare gases. Accurate potential curves for xenon excimers are obtained by comparison of two-photon spectra with line broadening theories. Selective quenching near potential crossings is observed in half-collision experiments where atoms absorbing in the red wing of a line are excited as collision pairs at a unique internuclear separation. In kinetic studies, excited state lifetimes, binary and three-body collisional deactivation rates are measured as well as state-to-state reaction rates for intramultiplet quenching. Experiments studying laser controlled reactive transfer are planned for xenon-chloride mixtures.

Texas A and M University
College Station, Texas 77843

276. X-Ray Emission in Heavy-Ion Collisions

R.L. Watson **$73,634**
Cyclotron Institute

Ionization, excitation, and electron transfer in high-energy heavy-ion collisions are under investigation by means of high resolution measurements of the photon radiation emitted during and after the collision process. The wavelength region of interest in these studies extends from the EUV up to x-rays in the KeV range. Current experimentation is directed toward (1) the spectroscopy of few-electron ions, including the determination of x-ray polarization associated with aligned states produced in the collision process; and (2) the systematic investigation of K x-ray satellite and hypersatellite structure, emphasizing the effects of rapid interatomic electron transfer.

University of Toledo
Toledo, Ohio 43606

277. Semiempirical Studies of Atomic Structure

L.J. Curtis **$32,000**
Department of Physics and Astronomy

The structure and properties of the very heavy and very highly ionized atoms that often occur as contaminants in controlled fusion devices are studied through experimental measurements, semiempirical data parameterizations, and *ab initio* computations. Laboratory observation and analysis of such spectra, often to parts-per-million accuracies, can exceed present theoretical capabilities, necessitating the development and extension of precision data systematizations into new high-Z regimes. Current emphasis is on the empirical study of quantities that are primarily sensitive to the inner portion of the wave function, which are often poorly described by *ab initio* methods that optimize the prediction of the gross energy. In some cases this has revealed subtle isoelectronic and homologous regularities not predicted by standard theoretical methods, which provide clues to the complex and highly relativistic inner core of many-electron ions, and can be exploited to obtain precise interpolative and extrapolative predictions. These predictions are tested using measurements by fast ion beam excitation, laser- and tokamak-produced plasmas, and conventional spectroscopic light sources; the results are used to sharpen predictions for subsequent measurement.

Vanderbilt University
Nashville, Tennessee 37235

278. Theoretical Studies of Atomic Transitions

C. Froese Fischer **$85,000**
Department of Computer Science

The present research is part of an ongoing project in atomic structure calculation, with special emphasis on the prediction of energy levels and transition probabilities as well as lifetimes. The method used is the MCHF method for including correlation effects in the wavefunction, optionally corrected for relativistic effects in the Breit-Pauli approximation. Transitions of current interest are the forbidden transitions, which may be important in astrophysics for the electron density, or which have been observed in tokamak plasmas. Also of interest are the transitions between the doubly excited states of calcium(II), where predicted wavelengths and lifetimes are needed to identify lines of observed spectra. The present general purpose programs for the study of bound-bound transitions are being extended to include photoionization studies which may be characterized as bound-continuum transitions.

University of Virginia
Charlottesville, Virginia 22901

279. ***Studies of Autoionizing States Relevant to Dielectronic Recombination***
T.F. Gallagher **$100,000**
Department of Physics

We use a novel laser excitation method to excite alkaline earth atoms in an atomic beam to autoionizing states that decay into an ion and a free electron. Our experiments are precisely the inverse of the dielectronic recombination of ions and electrons through autoionizing states, and thus allow detailed measurements of the basic physical processes important in dielectronic recombination. As dielectronic recombination is an important power loss process in tokamak plasmas, these insights have real practical value. We measure directly the total autoionization rates as a function of the principal and angular momentum quantum numbers and as a fucntion of applied electric fields. In addition, we measure the angular and energy distributions of the ejected electrons, which give us the autoionization rates into specific states of the ion and outgoing electrons. All together these measurements allow us to obtain the detailed microscopic atomic data that enter into the process of dielectronic recombination. This research has provided new insights into the basic physical processes important in dielectronic recombination.

Western Michigan University
Kalamazoo, Michigan 49008

280. ***Correlated Charge Changing Ion-Atom Collisions***
E.M. Bernstein, J.A. Tanis **$65,000**
Department of Physics

An experimental project probing fundamental interactions in ion-atom collisions is being conducted using accelerators at Brookhaven National Laboratory, Lawrence Berkeley Laboratory, and Western Michigan University. Individual inner-shell processes of excitation, ionization, and charge transfer are investigated for MeV/amu highly charged ions with atomic numbers in the range 12 to 26 incident on gas targets. This work is carried out by measuring coincidences between x-rays and the outgoing projectile charge state of interest. Cross sections are measured for several incident charge states for various projectile and target species. Specific topics being investigated or planned are: (1) resonant and nonresonant-transfer-and-excitation (RTE and NTE); (2) excitation and ionization of projectiles and targets; (3) total electron capture and loss by highly charged projectiles; (4) electron capture to excited states for hydrogen-like and fully-stripped projectiles; and (5) K- and L-shell radiative electron capture for highly charged ions. Work to date has provided significant new information on the systematics of RTE and its relationship to dielectronic recombination.

Chemical Energy

Brigham Young University
Provo, Utah 84602

281. ***Metal-Support Interactions: Their Effects on Catalytic Properties of Cobalt***
C.H. Bartholomew **$79,900**
Department of Chemical Engineering

Metal-support interactions and their effects on adsorption and activity-selectivity properties of cobalt are being investigated. The objectives of this study are: (1) to determine the effects of cobalt-support interactions on dispersion, oxidation state, and adsorption properties of cobalt; (2) to correlate the catalytic properties for hydrocarbon synthesis on cobalt with dispersion, oxidation state, and CO and H_2 adsorption properties; and (3) to measure directly the extent of interaction of various supports with iron and cobalt using Moessbauer spectroscopy. The work features a comprehensive, quantitative experimental investigation of cobalt on Al_2O_3, SiO_2, TiO_2, MgO, and carbon supports including careful characterization of the physical and chemical, bulk and surface properties of each catalyst with BET, H_2 and CO chemisorptions, XRD, TEM, TPD, and TPR measurements. Recent results provide evidence that dispersion and support significantly influence adsorption and CO hydrogenation activity-selectivity properties of cobalt.

University of California
Irvine, California 92717

282. ***Synthesis, Chemistry, and Catalytic Activity of Lanthanide Metals in Unusual Oxidation States and Coordination Environments***
W.J. Evans **$77,000**
Department of Chemistry

The objective of this project is to identify the special chemical properties of the lanthanide metals (14 heavy metals which are mined in California) and to exploit this unique chemistry to develop: (1) new materials of potential practical importance; (2) more efficient and more selective catalytic systems; and (3) new stoichiometric and catalytic reactions not presently possible with conventional catalysts. Our study of the chemistry of the lanthanide-carbon bond has led to the first molecules containing lanthanide-hydrogen bonds. These lanthanide hydrides catalytically activate molecular hydrogen, and we are studying the intermediates in this reaction to understand how to modify this reactivity in unusual ways. The reactions of the hydrides with nitriles, isocyanides, alkynes, and alkenes provide new, structurally unusual complexes whose chemistry is being examined. We have investigated the subtle factors having major effects on the rates of several of the above classes of four-center reactions. We have developed an efficient conversion of bimetallic hydrides to structurally unique trimetallic tetrahydrides and mixed metal intermetallic tetrahydrides, which may be of interest with respect to hydrogen storage. Oxide derivatives of these polymetallic hydrides, which may model oxide-supported heterogeneous catalysts, have been obtained.

University of California
Santa Barbara, California 93106

283. Homogeneous Catalysis of the Water Gas Shift Reaction
P.C. Ford **$83,000**
Department of Chemistry

Research is directed (1) toward elucidating fundamental mechanisms key to catalytic cycles including the water-gas shift reaction and (2) toward developing new homogeneous catalysts for such reactions. Studies in progress include kinetic investigations of important steps such as the nucleophilic activation of carbon monoxide coordinated to metal centers by a variety of species including the oxy anions HO^- and CH_3O^- ($M\text{-}CO + RO^- \rightarrow M\text{-}CO_2R^-$), the decarboxylation of hydroxy carbonyl adducts ($M\text{-}CO_2H^- \rightarrow M\text{-}H^- + CO_2$), the reductive elimination of H_2 from metal hydrides ($M\text{-}H^- + H_2O \rightarrow H_2 + M + OH$), and the substitution reactions of metal carbonyl complexes. Systems under investigation are largely drawn from those shown to have potential as homogeneous catalysts in the reactions of carbon monoxide. The elucidation of these mechanisms will provide guidelines for the molecular engineering of new and better catalysts for the production of fuels and other organic products from CO and other small molecule substrates.

284. Reactions of Iron Atoms with Molecules in Low Temperature Matrices
R.G. Pearson, P.H. Barrett **$74,800**
Department of Chemistry

The goal of this project is to study the reactivity of metal atoms and small clusters with molecules in low temperature matrices. Moessbauer and infrared spectroscopies are used to identify the reaction products. Reactions between iron, Fe_2, and iron clusters, and low temperature matrix isolated molecules of N_2, NO, CO, C_2H_4, and C_6H_6 have been studied and the products identified. This investigation includes the search for bond cleaving reactions of HX, some of which have been found. Reactions of CH_3X are also under study.

California Institute of Technology
Pasadena, California 91125

285. Fundamental Studies of Olefin and Acetylene Insertion Reactions
J.E. Bercaw **$80,000**
Department of Chemistry

This project involves fundamental studies of the mechanism and thermodynamics of olefin and acetylene insertion into metal-hydrogen and metal-carbon bonds. The reactions of olefins with hydride and alkyl derivatives of metallocenes of the general formulae $(\eta^5\text{-}C_5Me_5)_2ScR$ and $(\eta^5\text{-}C_5R'_5)_2M(\text{olefin})R$ (R = hydrogen, alkyl, alkenyl, alkynyl; R′ = hydrogen, Me; M = niobium, tantalum) have proven to be very clean and amenable to mechanistic studies. Relative ground state energies and structures for $(\eta^5\text{-}C_5R'_5)_2M(\text{olefin})H$ (M = niobium, tantalum; R′ = hydrogen, Me) are being determined by competitive olefin binding studies and by examination of their molecular structures. Relative transition state energies are established by measuring insertion rates as a function of olefin substituent electronics and sterics. The kinetics of step-wise insertion of ethylene into the scandium-carbon bonds of $(\eta^5\text{-}C_5Me_5)_2Sc\text{–}R$ (R = hydrogen, alkyl, alkenyl, alkynyl) is being examined by ^1H, ^2H, and ^{13}C NMR spectroscopy. These processes (olefin insertion into the metal hydride bond, its reverse β-H elimination, and the related process insertion into the metal alkyl bond) are among the most important steps in homogeneously catalyzed reactions of olefins.

286. Organometallic Catalysts and Analogs for CO Reduction and Carbon-Carbon Bond Cleavage Reactions
R.H. Grubbs **$111,000**
Department of Chemistry

The research is concerned with the activation and reduction of carbon monoxide and the development of models for the assembly of hydrocarbons on multimetal catalysts. Group VI-B intramolecular metalloesters are synthesized from cationic transition-metal(II) carbonyl complexes, employing intramolecular nucleophiles. Spectroscopic and x-ray crystallographic evidence confirm the general structure as an ester derived from the attack of an alkoxide at a carbonyl ligand. Equilibrium studies indicate that attack by an intramolecular nucleophile may be favored over that of an intermolecular one depending on the structure linking the nucleophile to the metal center. The optimum linker configuration and oxidation state for intramolecular nucleophilic attack is being investigated. A family of Group IV ketene complexes has been synthesized as models for C–C coupling intermediates in CO reduction reactions. Of particular interest are hetero-binuclear complexes which show a wide range of reactivities and structures. The first case of a trigonal bipyrimidal CH_3M_2 complex has resulted from these studies. A large number of $M\text{-}CH_2$ complexes have been prepared and demonstrated to undergo a variety of C–C coupling reactions.

University of Chicago
Chicago, Illinois 60637

287. Reactions of Electrophilic Reagents with Bituminous Coals: The Chemistry of the Reaction Products
L.M. Stock **$87,400**
Department of Chemistry

We have concentrated on the ruthenium(VIII) catalyzed oxidation of coal. The phenolic and etherol aromatic molecules are selectively oxidized in this process to yield simpler structures. The products derived from 20 representative molecules have been worked out, and the products from several representative coals have been studied by mass spectrometry. In addition, quantitative methods based upon isotopic dilution techniques have been worked out and applied successfully for the determination of the methyl groups and other prominant structural features in coal. This information can be used to predict the quantity of methane expected during low severity pyrolyses. The electrophilic reactions of bituminous coals are under investigation. Early work on the plumbylation reaction of Illinois No. 6 coal yields a product that undergoes oxidative solvolysis to yield a material selectively enriched in aryl hydroxyl groups. This altered coal undergoes donor solvent liquefaction in tetralin to yield products that are more soluble in hexane than the natural materials. This work should provide a more secure basis for the discussion of the role of hydroxyl groups on coal conversion, thus enabling their greater control.

University of Colorado
Boulder, Colorado 80309

288. *Studies of New Elimination Reactions of Metal Complexes*
M.R. DuBois **$59,000**
Department of Chemistry

This project investigates elimination and rearrangement reactions of the hydrocarbon portions of thiolate ligands in dimers of the general types $[CpMo(\mu\text{-}S)\mu\text{-}SR]_2$ and $[CpMo(\mu\text{-}SR)_2]_2$. One area of focus has been an investigation of the reactivity of deuterium with bridging alkenedithiolate ligands in molybdenum (III) dimers of the formula $(CpMo)_2$ (SCRCRS) (S_2CH_2). The complexes are prepared by the addition of an alkyne to the sulfido ligands in $(CpMo)_2$ $(\mu\text{-}S)_2$ (S_2CH_2). In the reaction of the alkyne adducts with deuterium, two competitive processes occur: (1) deuterium substitution onto the carbon atoms, which are alpha to the double bond and (2) *cis* addition of deuterium to the double bond. The resulting deuterated alkanedithiolate ligand undergoes carbon–sulfur bond cleavage to release the *cis* alkene with varying degrees of deuterium substitution. Examples of the products with maximum deuterium incorporation include perdeuteropropene prepared from the propyne adduct, perdeutero *cis-2-butene* from the 2-butyne adduct, and d^7 *cis-2-pentene* from the 2-pentyne adduct. GC-MS characterization of the last product indicates that the methyl group, which is beta to the double bond, remains undeuterated. The yields of the products with maximum deuterium incorporation vary depending on reaction conditions, including temperature and the concentration of free alkyne.

289. *Promoter Modifications of Catalytic Activity and Selectivity*
J.L. Falconer **$60,000**
Department of Chemical Engineering

The effects of alkali promoters on the activity and selectivity for CO and CO_2 hydrogenation are being studied on supported metal catalysts, using the techniques of temperature-programmed desorption, reaction, and decomposition. Differential kinetic studies, static chemisorption, and x-ray photoelectron spectroscopy are also used. The support has a strong influence on the changes induced by the addition of promoter. These changes are due in part to the interaction of the promoter with the support, so that the promoter/metal ratio is not sufficient to characterize the catalyst. Thus the effect of varying both the metal and the promoter loadings are being studied. Rates of individual reaction steps are being measured with temperature-programmed reaction; alkali promoters decrease the rate of carbon hydrogenation and weaken the hydrogen bond to the surface. Preparation method has little effect on the kinetics, but calcination increases higher olefin selectivities. Unusual effects of reduction and of reaction temperature are observed on promoted nickel powders.

Colorado State University
Fort Collins, Colorado 80523

290. *Chemically Modified Electrodes and Related Solution Chemistry*
C.M. Elliott **$73,500**
Department of Chemistry

In this research we are investigating chemically modified electodes and related solution chemistry. The goal is to alter the chemical and/or physical properties of the electrode-solution interface in useful ways. One interest is catalyzing reactions of various kinetically inert small molecules (e.g., the reduction of dioxygen and dinitrogen and the oxidation of hydrocarbons). Different synthetic procedures appropriate for each material under study are investigated in order to chemically bind the molecules of interest to the surfaces of bulk electrode materials. Our primary emphasis is the development of polymer coated electrodes containing electroactive materials. Several such electrodes have been prepared. We are studying the fundamental processes of electron and ion transport in such modifying polymers. A number of novel metalloporphyrins have been prepared, and their redox chemistry is under investigation both in solution and polymer-bound. Other polymers under study have novel electrochromic and redox-adjustable ion exchange properties. The primary methods of investigation of these surfaces are electrochemical, including such techniques as chronoamperometry, cyclic voltammetry, and rotated disk voltammetry.

291. *Diosmacycloalkanes as Models for the Formation of Hydrocarbons from Surface Methylenes*
J.R. Norton **$63,272**
Department of Chemistry

This project has developed several efficient general syntheses of diosmacycloalkanes. The project will next determine the extent to which these compounds can: (1) serve as models for methylene aggregation on the surface of Fischer-Tropsch catalysts; (2) catalyze olefin metathesis; and (3) rearrange carbon skeletons. The properties of these compounds will be compared to those of their mononuclear analogs, in order to determine which (if any) steps in typical catalytic sequences require the presence of polynuclear systems. The project will also see if hydrocarbon C–H bonds can be activated by $Os(CO)_4$ or any other species generated photochemically from $Os(CO)_5$.

292. *Reactions of Alkyl Palladium and Platinum Dimers: Mechanisms of Dinuclear Elimination*
J.K. Stille **$71,500**
Department of Chemistry

The transmetallation reaction of trimethylaluminum with the palladium(I) chloride dimer, $Pd_2Cl_2(\mu\text{-dppm})_2$ [dppm = bis (diphenylphosphino) methane] at -78°C yields an intermediate Pd_2ClMe $(\mu\text{-dppm})_2$, in which one of the chlorines has been replaced by methyl. This intermediate disproportionates on warming to give the palladium(II) dimer, $Pd_2Cl_2Me_2$ $(\mu\text{-dppm})_2$, and a palladium(0) dimer. The reaction of Pd_2ClMe $(\mu\text{-dppm})_2$ with ethanol at -78°C gives relatively stable A-frame chlorobridged dimer $[Pd_2HMe(\mu Cl)\ (\mu dppm)_2]^+$ containing a hydride on one palladium and a methyl on the other (x-ray). On warming in solution this dimer loses methane to yield Pd_2Cl_2 $(\mu\text{-dppm})_2$. If Pd_2ClMe $(\mu\text{-dppm})_2$ is first warmed to -48°C and then treated with ethanol, an A-frame hydridobridged dimer $[Pd_2Me_2(\mu\text{-}H)\ (\mu\text{-dppm})_2]^+$ containing methyls on each palladium is generated. This dimer in solution also loses methane on warming.

University of Connecticut
Storrs, Connecticut 06268

293. *Highly Dispersed Metal Atoms in Zeolites*

S.L. Suib **$109,600**
Department of Chemistry **(24 mo.)**

The purpose of this project is to understand ways of producing small particles of highly reduced metals in zeolites. Current emphasis is on the effect of microwave discharge methods for the synthesis of highly dispersed metal atoms in zeolite pores. We are working with iron, cobalt, and nickel. The microwave discharge procedure provides a general method to produce small metal particles on other supports such as SiO_2, Al_2O_3, polymers, and TiO_2. Characterization of these materials involves Moessbauer spectroscopy, ferromagnetic resonance, x-ray powder diffraction, and surface analyses with Auger, x-ray photoelectron spectroscopy, ion scattering spectroscopy, and secondary ion mass spectroscopy. Superparamagnetic iron (0) and cobalt (0) clusters less than 20 Å in size are prepared. Another aspect of this research involves use of these zeolites in Fischer-Tropsch and methanation reactions.

University of Delaware
Newark, Delaware 19716

294. *A Surface Science Investigation of Potential Intermediates, Catalysts, and Promoters in the Synthesis of Higher Alcohols by Metals*

M.A. Barteau **$64,200**
Center For Catalytic Science and Technology

The goal of this project is to provide the fundamental knowledge required to extend recent advances in methanol synthesis catalysis to the development of selective noble metal catalysts for the synthesis of higher alcohols. The hypothesis is that surface alkoxide species are pivotal intermediates in the synthesis of higher alcohols. This study examines the formation, stability, and reactivity of these intermediates on clean and modified surfaces of rhodium and palladium in order to determine the properties of these metals that lead one (rhodium) to be active for synthesis of higher alcohols. By studying the influence of inorganic surface promoters upon alkoxide reactivity, we will determine the ability of promoters to alter the intrinsic catalytic properties of these metals, and probe the importance of promoter electronegativity in the modification of surface reactivity. The reactions of C_1–C_4 alcohols are studied with a battery of essential surface spectroscopic techniques, including TPD, HREELS, UPS, and XPS.

Harvard University
Cambridge, Massachusetts 02138

295. *Model Studies of Hydrodesulfurization and Hydrodenitrogenation on Sulfided Molybdenum Surfaces*

C.M. Friend **$75,700**
Department of Chemistry

This project is a study of hydrodenitrogenation and hydrodesulfurization reactions under model conditions on single-crystal molybdenum surfaces. Studies will be performed both in ultra-high vacuum and in a high-pressure (1 atm) transfer cell currently under construction. Preliminary studies have focused on the study of sulfur-containing cyclic hydrocarbons adsorbed on molybdenum(110) under ultra-high vacuum conditions primarily utilizing thermal desorption spectroscopy in conjunction with isotopic labeling experiments. The importance of hydrogenation prior to carbon–sulfur bond cleavage is being investigated by characterizing the chemistry of partially and completely hydrogenated C_4SH_m molecules ($m = 4$ to 8). The chemistry of C_2- and C_3-rings is also under investigation. Spectroscopic studies (NEXAFS and HREELS) aimed at identifying adsorption structure will follow.

Indiana University
Bloomington, Indiana 47405

296. *Metal Aldoxides: Models for Metal Oxides*

M.H. Chisholm **$77,000**
Department of Chemistry

Structural analogies between polynuclear metal alkoxides and metal oxides have been noted, with the former providing models for subunits within the extended networks of the latter. An extensive organometallic chemistry supported by alkoxy ligands is emerging. Their facile interconversion between terminal and bridging positions and between σ^2 and $(\sigma^2 + \pi^2)$ donors allows for easy uptake and release of substrate molecules. Key observations during the 1984 to 1985 period are: (1) the cleavage of $C=O$ to carbido and oxo tungsten alkoxide clusters; (2) the coupling, co-coupling, and sometimes metathesis-like reactions ($M = W$) between $C\equiv C$, $C\equiv N$, and $M\equiv M$ bonds in $M_2(OR)_6$ compounds; (3) unusual β-hydrogen effects in dinuclear alkylalkoxides of molybdenum; and (4) the isolation of Mo–Mo quadruply bonded compounds supported by alkoxide ligands. Recent developments have led to general sysnthesis of hydridoditungsten alkoxide anions $W_2(\mu\text{-H})(OR)_8^-$, which have been isolated as sodium salts. New nitrido and amido clusters have been discovered, $Mo_4(\mu_3\text{-N})_2(OPr^i)_{12}$ and $W_3(\mu_3\text{-NH})(OPr^i)_{10}$, which may provide models for the Haber synthesis of NH_3 from N_2 and H_2.

297. *Radical Chain and Rearrangement Reactions in Coal Liquefaction*

J.J. Gajewski, K.E. Gilbert **$75,000**
Department of Chemistry

The project focuses on the fundamental mechanistic problems involved in the thermal reactions of hydroaromatic compounds that may serve as a basis for understanding the chemistry of coal liquefaction. We have found that 1,3-diarylhydrocarbons and ethers decompose by free radical chain processes at 300 to 400°C, that these reactions may be initiated at lower temperatures, and may be inhibited by hindered phenols up to 200°C. The kinetic and thermodynamic barriers to these reactions have been studied. We have found that phenyl substituted tetralins cleave to smaller fragments by a complex series of radical reactions that are very inefficient. We have also found that alkenes can be hydrogenated to alkanes in good hydrogen donor solvents, but react to form dimers and higher molecular weight materials in poor hydrogen donor solvents at 300°C.

Indiana University–Purdue University
Indianapolis, Indiana 46223

298. *Studies of Metal–Ammonia Interactions with Aromatic Substrates*
P.W. Rabideau **$63,000**
Department of Chemistry

Reduction and reductive alkylations effected by electron addition in dissolving metal systems such as sodium or lithium in liquid ammonia can provide an important method for the solubilization of coal and studies of coal structure. This research is aimed at a better understanding of the fundamental nature of this reaction using aromatic and polynuclear aromatic compounds as model structures. Recently, dimeric methylated naphthalene derivatives have been used as coal models; it has been determined that the presence of a second polynuclear ring system does not inhibit reduction of the first, but rather it seems to promote it. The significance is that a first approximation coal can be thought of as a large number of polynuclear ring systems linked together by carbon chains. The intermediates in these reactions are being studied directly by carbon and proton nuclear magnetic resonance techniques, and indirectly by protonation sites and alkylation stereochemistry. The conformational analysis of the reduced products (partially reduced six-membered rings) is also being studied by NMR techniques as well as theoretically with force field calculations.

University of Kentucky
Lexington, Kentucky 40506

299. *Metallacumulenes and Carbide Complexes*
J.P. Selegue **$60,000**
Department of Chemistry

We are preparing and characterizing a series of metallacumulene and carbide complexes, containing cumulated chains of carbon–carbon double bonds terminating at transition metal atoms at one or both ends. Complexes under study include vinylidenes ($M{=}C{=}CR_2$), poly(vinylidenes) ($M(C{=}CR_2)_n$, n = 2, 3, 4), allenylidenes ($M{=}C{=}C{=}CR_2$), butatrienylidenes ($M{=}C{=}C{=}C{=}CR_2$), ketenylidenes ($M{=}C{=}C{=}O$), propadienonylidenes ($M{=}C{=}C{=}C{=}O$) and their imino and thio analogs, μ_2-carbides ($M{=}C{=}M$) and bicarbides ($M{=}C{=}C{=}M$). We are using $[M(PR_3)_2(Cp)]$ (M = iron, ruthenium, osmium), $[M(CO)_2(Cp)]$ (M = manganese, rhenium), $[M(PR_3)_4]$ (M = molybdenum, tungsten), and other metal moieties to stabilize the cumulated ligands. These complexes serve as models for carbon-rich fragments that are bound to metal catalyst surfaces during synthesis gas and acetylene conversion reactions. The compounds are characterized by spectroscopy and x-ray diffraction. Their chemical reactivity toward H_2, CO, H^+, OH^-, and other simple substrates is being surveyed to assess their suitability as models for reactive intermediates.

Lehigh University
Bethlehem, Pennsylvania 18015

300. *Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane*
K. Klier, G.W. Simmons, **$115,000**
R.G. Herman, J.E. Sturm
Department of Chemistry

This project will investigate the scientific foundations for processes dealing with selective oxidation of methane to methanol and formaldehyde. Progress is in two major areas. First, catalytic oxidation of methane to formaldehyde by molecular oxygen over molybdena-based catalysts at subatmospheric pressures: the process conditions for the selective production of formaldehyde have been identified and the yields obtained with oxygen have been found to be comparable to the yields reported in the literature using nitrous oxide as the oxidizing agent. The catalysts have been characterized by laser Raman microprobe, electron microscopy, EPR, and ESCA/Auger spectroscopy. Second, surface science of adsorbates in the palladium–oxygen–dichloromethane–methane system: a combined LEED/Auger/Mass spectrometer apparatus dedicated to this project has been constructed and is in operation. The structures, energetics, and desorption patterns of oxygen and dichloromethane overlayers have been determined on the palladium(100) crystal surface. An interesting exclusion of dichloromethane chemisorption by preadsorbed oxygen and the occurrence of oxygen chemisorption into the dichloromethane overlayer have been observed. These results indicate a reaction pattern that will be very sensitive to the gas phase oxygen-to-dichloromethane concentration ratio. A separate high resolution electron energy loss spectrometer (EELS) is in advanced stages of construction.

301. *Polymer-Based Catalysts*
S.L. Regen **$126,000**
Department of Chemistry **(24 mo.)**

This research is aimed at developing highly active and stable polymeric catalysts for use in aqueous–liquid organic two-phase and aqueous–resin–liquid organic three-phase reactions. Current effort is focusing on poly(ethylene glycols) and poly(ethylene glycol)-grafted copolymers as catalysts for promoting dehydrohalogenation, alkylation, and saponification processes. Preliminary results indicate that significantly improved synthetic procedures are possible based on such catalysts, which should be amenable for a variety of laboratory and industrial applications.

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

302. *Reduction of Carbon Monoxide*
R.R. Schrock **$115,000**
Department of Chemistry

The objective of this research is to learn how to reduce carbon monoxide catalytically and selectively to a two-carbon product such as ethanol, ethylene glycol, ethylene, or acetaldehyde. The approach is to discover how earlier transition metal hydride complexes can take part in unique reactions not possible with the later transition metals (i.e., what new principles of catalytic reduction of carbon monoxide remain to be discovered). The project involves the synthesis of new transition metal hydrido complexes and a detailed study of how they react with carbon monoxide to give a μ-hydrido μ-formyl species. Analogous reactions employing less oxophilic metals are being sought. At present, we are investigating some novel tungsten hydrido clusters and complexes containing linked cyclopentadienyl ligands, including a late/early transition metal combination. The late/early transition metal complex is being tested for activity under typical syngas conditions.

University of Minnesota
Minneapolis, Minnesota 55455

303. *Direct Alcohol Synthesis on Cobalt Modified Catalysts*

G.L. Griffin **$76,600**
Department of Chemical Engineering and Materials Science

We will study the adsorption and reaction properties of Cu-ZnO, Co-ZnO, and Co-Cu-ZnO catalysts intended for the direct synthesis of methanol and higher alcohols. The principal goals are (1) to understand the adsorption behavior of highly dispersed metal cations in ZnO-based catalysts; (2) to determine the importance of these adsorption sites in alcohol synthesis reactions; and (3) to test whether dispersed Co-ZnO or Co-Cu-ZnO catalyst might provide efficient catalysts for the direct synthesis of ethanol, perhaps via the methanol homologation reaction. Adsorption measurements, including IR spectroscopy and temperature programmed desorption, will be combined with kinetic experiments to obtain a unified picture of the behavior of these catalysts. This research will improve our understanding and control of direct synthesis reactions on multifunctional catalysts. The long-range benefit will be to elucidate the catalytic behavior and stability of highly dispersed transition metal cations on oxide supports.

304. *Photochemical Properties of Transition Metal-Arene Complexes*

K.R. Mann **$133,900**
Department of Chemistry **(24 mo.)**

The photochemical reactivity of transition metal-arene complexes will be studied by examining the mechanisms of the arene replacement reactions by NMR, laser flash photolysis, and classical mechanistic techniques. The intermediate species generated in these reactions will be utilized as catalytic photoassistance agents, and in the synthesis of novel organometallic complexes.

National Bureau of Standards
Gaithersburg, Maryland 20899

305. *Structure and Reactivity of Chemisorbed Species and Reaction Intermediates*

T.E. Madey **$132,300**
Surface Science Division

This project addresses the structure and reactivity of adsorbed molecules on single-crystal catalysts and on high-area catalysts using a variety of experimental methods. During the last year, research has involved four areas with a common theme, the investigation of surface processes related to catalytic chemistry. The role of surface additives (oxygen, bromine, sodium, potassium) on the local structure and surface chemistry of small molecules (NH_3, CO) adsorbed on single-crystal metal surfaces (ruthenium, iron, silver) was studied using the electron stimulated desorption ion angular distribution (ESDIAD) method. The additives often were found to induce new structural forms of the adsorbed molecules and reaction products. The adsorption and decomposition of CO and O_2 on a chromium(110) surface were characterized using high resolution electron energy loss spectroscopy (EELS); molecular precursors to decomposition were found in both cases. Neutron inelastic scattering (NIS) was used to measure the vibrational spectra of hydrogen and hydrocarbons adsorbed on surfaces of platinum-black and zeolite catalysts. Hydrogenation and hydrogenolysis reactions were studied over single-crystal tungsten(110) and over tungsten(100) dosed with fractional monolayers of platinum. The role of surface carbide was found to be critical to the reaction mechanism.

University of North Carolina
Chapel Hill, North Carolina 27514

306. *The Heats of Formation of Gas Phase Organo-Sulfur Molecules and Applications of ^{17}O and ^{33}S NMR to Structure Determinations*

T. Baer, S.A. Evans, Jr. **$73,808**
Department of Chemistry

This project emphasizes photoionization and heteronuclear nuclear magnetic resonance (NMR) techniques directed toward the determination of structures and energetics of organosulfur molecules. The ΔH_f^0 of the series: $RS \cdot$ [$R = CH_3$, CH_3CH_2,$(CH_3)_2CH$, and $(CH_3)_3C$] are being measured. In addition, the ΔH_f^0 of various sulfonyl compounds are being determined by bomb calorimetry to make these substances amenable for photoionization studies. Chemical oxidation of sulfenyl sulfur (-S-) to sulfones ($-SO_2-$) and particularly, to sulfonic acids ($-SO_3H$) serves to "quench" the quadrupolar broadening effect. This allows for the development of an analytical NMR technique for the rapid and accurate analysis of sulfur in organosulfur constituents in coal and petroleum extracts. Polar substituent effects on ^{33}S chemical shifts in aryl sulfones and sulfonic acids are being evaluated, as well as the possible use of magic-angle spinning techniques for determination of ^{33}S shift parameters in the solid state.

307. *Reductive Coupling of Carbon Monoxide to C_2 Products*

J.L. Templeton **$60,000**
Department of Chemistry

This project presents a new mechanistic approach to C_2 syngas products: reductive C-C bond formation between adjacent carbon monoxide ligands at a single metal center. We will build on two distinct conceptual approaches. The first will employ external reductants in an effort to reductively couple cis-carbonyl ligands to form $[OC \equiv CO]^{-2}$, which could be protonated to yield a bound acetylenediol. The acute OC-M-CO angles of seven-coordinate d^4 metal carbonyl derivatives and the anticipated six-coordinated d^4 alkyne containing products seem uniquely suited for realizing this chemistry. The second approach focuses on the conversion of a terminal CO to a pseudocarbyne by protonation (or Lewis acid addition) at the oxygen to generate an effective hydroxycarbyne cis to a carbonyl. Two examples of a carbyne-carbonyl coupling have been reported. We intend to promote a similar internal redox process by addition of acid and free ligand to convert d^6 $L_4M(CO)_2$ to $L_4L'M(HOC \equiv COH)$ or a Lewis acid analog.

Northwestern University
Evanston, Illinois 60201

308. *Solid State, Surface, and Catalytic Studies of Oxides*

H.H. Kung **$86,500**
Department of Chemical Engineering

The purpose of this project is to elucidate the interrelation among the solid state, surface, and catalytic properties of oxides. Selectivity for butadiene in the oxidation of butene was used to probe the different catalytic properties of α- and γ-Fe_2O_3 that differ in their bulk structure. It was found that γ-Fe_2O_3 is more selective for butadiene than α-Fe_2O_3. The difference can be attributed to the fact that the product butadiene binds more weakly and the adsorbed hydrocarbon intermediates are less sensitive to gas phase oxygen degradation on γ-Fe_2O_3 than on α-Fe_2O_3. The role of the surface structure in determining surface chemistry is studied with different crystal faces of ZnO. From temperature programmed decomposition experiments using various oxygenates, it is found that the different surface properties of various surfaces can be attributed to the different magnitudes and orientation of surface dipole moments, different degrees of ionicity of the surface zinc ions, and different degrees of steric hindrance of surface zinc ions for the different surfaces. Finally, research on the kinetics in methanol synthesis on Cu-Zn oxide catalysts led to the discovery that nonequilibrium thermodynamic theory can be used to treat relaxation of reaction systems near equilibrium. This permits the determination of reaction rates in systems where there are more independent chemical reactions than independent chemical species.

309. *Supported f-Element Organometallic Complexes: Surface Chemistry and Catalysis*

T.J. Marks, R.L. Burwell, Jr. **$71,000**
Department of Chemistry

This project involves an integrated chemical-spectroscopic investigation of surface chemistry and heterogeneous catalysis by lanthanide and actinide organometallic complexes adsorbed on high surface area metal oxides. A detailed chemical study of the adsorption of $Cp'_2M(CH_3)_2$ and $CP'_2M(CD_3)_2$ ($Cp' = (CH_3)_5C_5$, M = thorium, uranium) on aluminas of varying -OH or -OD coverage evidences a multiplicity of molecule-surface reaction pathways. Complementary high resolution surface ^{13}C NMR spectroscopic data support these conclusions and demonstrate transfer of methyl groups from the actinide molecules to surface aluminum ions. When adsorbed on dehydroxylated alumina, these organoactinide molecules are very active catalysts for propylene hydrogenation and ethylene polymerization. Poisoning experiments indicate that only a few percent of the adsorbed molecules exhibit this high activity. It is also found that the complexes $Cp'_2Th(neopentyl)_2$ and $(Cp'_2ThH_2)_2$ have comparable activity for propylene hydrogenation while $Cp'Th(benzyl)_3$ is far more active and $Cp_3Th(n\text{-}butyl)$ ($Cp = C_5H_5$) is far less active. Adsorption of the $Cp'_2M(CH_3)_2$ complexes on partially dehydroxylated alumina or silica gel produces far less active catalysts. This observation can be correlated with chemical and spectroscopic evidence for extensive $M\text{-}CH_3$ bond protonolysis.

310. *Chemical Interactions in Bimetal/Zeolite Catalysts*

W.M.H. Sachtler **$86,600**
Department of Chemistry

The industrial application of transition metals, supported by zeolites, is limited by the weak metal/support interaction of these systems, which results in poor dispersion maintenance of the metal under severe conditions. The primary project objective is to increase the dispersion maintenance by introducing a chemical anchor for the noble metal. We have found that the cations Fe^{2+} and Cr^{3+}, when exchanged into a NaY zeolite, markedly improve the dispersion of platinum. One test is to first oxidize $Pt(NH_3)_4{}^{2+}$/NaY in O_2, increasing the temperature from 20 to 550°C and then to reduce the metal with H_2 at 550°C. After this severe treatment the platinum particle size is measured by x-ray diffraction (XRD) and H_2 chemisorption. Both methods reveal a significant anchoring effect of Fe^{2+} and Cr^{3+} ions; in their absence large XRD signals of platinum are recorded, but with Fe^{2+} no platinum XRD signal can be detected, and a superior dispersion is maintained after 100 hours in H_2 at 500°C. Benzene hydrogenation revealed that the platinum catalyzed reaction rate was dramatically increased. This increase in rate exceeded the increase in platinum dispersion by a factor of seven. We are employing EXAFS to investigate the interaction between platinum particles and chemical anchor ions. We plan to use other transition metal ions and other test reactions (conversion of n-hexane or methyl-cyclopentane) in order to identify the dual action of transition metal ions as anchors and catalyst promoters.

311. *Structure and Chemistry of the Interaction of Organometallics with Surfaces*

D.F. Shriver **$99,500**
Department of Chemistry

One objective of this research is to characterize organometallics attached to surfaces with the purpose of elucidating the cluster-support interaction. Parallel model studies of organometallic compounds in solution and of conventionally-prepared heterogeneous catalysts are being performed to obtain a coherent picture of fundamental organometallic chemistry related to CO activation by heterogeneous catalysts. Based on our previous experience with the chemistry of CO in homogeneous solution chemistry, we have postulated that electropositive metals promote CO cleavage and migration insertion reactions. Therefore, we are studying supported mixed-metal clusters that contain one electropositive metal (e.g., Rh-Fe clusters on metal oxide surfaces by infrared and EXAFS techniques). The catalytic chemistry of these same materials is under investigation.

Owens-Illinois, Inc.
Toledo, Ohio 43666

312. *Investigation of the Nature of Semisynthetic Esterases*

M.H. Keyes **$74,900**
Department of Biotechnology

This project is designed to study the nature of semisynthetic esterases, generated from nonesterase proteins, by means of conformational modifications induced by inhibitors of natural esterases. Two esterases are being generated from bovine pancreatic ribonuclease, after perturbing the protein under acid pH, using indolepropionic acid as the modifier and cross-linking with glutaraldehyde. The esterase activity is assayed using tryptophan ethyl ester as substrate and measuring the ethanol produced. The two esterases are distinguished by their distinct pH optima, substrate specificity, and inhibition by tryptophan. After separation by ammonium sulfate precipitation, purification of the esterases is accomplished via gel filtration. The specificity of the esterases is being investigated using various esters and amide substrates. Kinetic studies on the most appropriate substrates are being conducted. Further purification of the esterases is being pursued.

University of Pennsylvania
Philadelphia, Pennsylvania 19104

313. Desorption and Reaction Kinetics Studied on Model Supported Catalysts

R.J. Gorte **$80,000**
Department of Chemical Engineering

Temperature programmed desorption (TPD) and reaction studies are proposed on model catalysts in which platinum or palladium are deposited on flat oxide substrates of alumina, silica, and zirconia. Average particle sizes will be calculated from the weight of metal deposited on the substrate as measured by a quartz-crystal film thickness monitor and from the TPD saturation area. TPD spectra of CO and H_2 from platinum and palladium on different supports will be measured to determine why catalytic activity varies for some reactions on these supports. Reaction studies for a hydrogenolysis reaction will be measured to determine whether structure sensitivity is likely to be related to the observed support effects. Reaction and TPD results from the different substrates will be correlated to determine how the substrate affects the catalytic activity.

314. Catalytic Hydrogenation of Carbon Monoxide

B.B. Wayland **$183,000**
Department of Chemistry **(24 mo.)**

The principal objective of this project is to learn how to use the unique properties of rhodium porphyrins in achieving catalytic hydrogenation of carbon monoxide at mild conditions. Rhodium porphyrins react with H_2 and CO at pressures < 1 atm to produce the first intermediate in the hydrogenation of CO and provide a realistic opportunity to participate in the catalytic hydrogenation of CO at low gas pressures. Several catalytic schemes are proposed which take advantage of the unique reactivity of rhodium porphyrins coupled with the aldehyde-like character of the metalloformyl intermediate. Multifunctional catalysts that utilize rhodium porphyrins and a second catalyst known to promote the hydrogenation of aldehydes are particularly promising candidates for achieving low pressure hydrogenation of CO. Solvent effects will be explored as one means for tuning the thermodynamic and kinetic parameters for optimum catalytic behavior. Comparative studies utilizing variation of the macrocycle and central metals (cobalt, rhodium, iridium) are being used in identifying the essential features required to obtain a catalyst system based on metallo macrocyles.

Pennsylvania State University
University Park, Pennsylvania 16802

315. Mechanistic Studies of Carbon Monoxide Reduction

G.L. Geoffroy **$105,000**
Department of Chemistry

Mechanistic schemes for the metal surface catalyzed reduction of carbon monoxide to methanol and to hydrocarbons have been proposed; the feasibility of these mechanisms is being tested by preparing and studying the chemistry of metal clusters that resemble the proposed surface intermediates. Recent focus has been on studies of the reactivity of the methylene cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$, (1). Cluster (1) reacts with CO to give the ketene cluster $Os_3(CO)_{11}(\mu\text{-}CH_2CO)$ and with halides to give a series of $[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)]^-$ clusters. The latter all react with CO to give ketene derivatives with rates 10^2 times faster than does (1), illustrating a novel example of halide promotion of CO insertion. Reasons for the latter are currently under study as are other synthetic routes to ketene clusters. Also being explored is the derivative chemistry of the ketene ligands in these complexes. For example, the ketene ligand in $[Os_3(CO)_{10}(\mu\text{-}I)\text{-}(\text{-}CH_2CO)]^-$ reacts with H^+ to give the μ-acetyl cluster $Os_3(CO)_{10}(\mu\text{-}I)\text{-}(\mu\text{-}O{=}CCH_3)$ and with CH_3^+ to give a vinyl derivative.

316. Transition Metal Catalyzed Transformations of Unsaturated Molecules

A. Sen **$156,000**
Department of Chemistry **(24 mo.)**

The homogeneous catalysis of organic transformations by transition metal compounds is of considerable practical and scientific importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The project objectives are (1) to achieve a fundamental mechanistic understanding of a number of important homogeneous catalytic systems and (2) to use this knowledge to develop new and useful catalytic processes. The two catalytic systems under current study are: (1) the palladium(II) and rhodium(I) catalyzed copolymerization and cooligomerization of olefins with carbon monoxide and (2) the palladium(II) catalyzed tail-to-tail dimerization of alkyl acrylates. For the former system our studies have resulted in elucidation of the unique chain-growth mechanism. Current focus is on further mechanistic studies of the individual steps in the chain-growth sequence and examination of the scope of the copolymerization reaction. Regarding the later catalytic system, current reactivity studies are of compounds that model the possible intermediates.

317. Metal-Support Interactions in Nickel, Palladium, and Platinum Catalysts

M.A. Vannice **$94,000**
Department of Chemical Engineering

This research seeks to elucidate the chemistry involved in the creation of metal-support interactions that have pronounced effects on adsorption and catalytic behavior in certain systems (presumed to be due primarily to modifications of the adsorbed state of reactant molecules). This project focuses on characterizing adsorbed molecules and the chemical and physical state of the metal and support. The project involves a study of heats of adsorption and desorption energies for H_2, CO, and O_2 on platinum, palladium, and nickel, using a modified differential scanning calorimeter combined with a thermal gravimetric analysis unit. Separate chemisorption experiments are to be conducted in a volumetric adsorption system, and kinetic investigations will be made on the hydrogenation of carbon monoxide and aromatic hydrocarbons. A new scanning transmission electron microscope system will be used to better define the state of the metal particles and the particle size distributions. Solid-state magic angle spinning NMR will be used to study adsorbed ^{13}C-labeled CO and hydrocarbons and to conduct Knight shift experiments on the metal itself (^{195}Pt) to determine the influence of the support on conduction electrons. ESR studies will be initiated to examine reduced TiO_2 and the formation of Ti^{3+} cations, in particular. This multifaceted approach attempts to explain both the much higher catalytic activities found in certain reactions and the suppressed chemisorption sometimes observed after a high-temperature reduction. A recently proposed model invoking special active sites created at the metal support interface will be carefully examined.

University of Pittsburgh
Pittsburgh, Pennsylvania 15261

318. *Carbidic Ad-Layer as Rate Controlling Factor in CO-H₂ Catalysis*

P. Biloen **$81,000**
Department of Chemical and **(24 mo.)**
Petroleum Engineering

The objective of this project is to assess the reactivity and abundance of reaction intermediates present at the surface of $CO-H_2$ converting catalysts during steady-state catalysis. The central question being addressed is to what extent carbonaceous side products control the abundancy of reaction intermediates. In a typical experiment, the isotopic constitution of the feed is being changed abruptly (e.g., $^{12}CO-H_2 \rightarrow {}^{13}CO-H_2$). This leads to a transient phenomenon: the displacement of ^{12}C by ^{13}C, first in the catalyst ad-layer and then in the product. The rates of displacement contain transient-kinetic information regarding the abundancy and reactivity (i.e., lifetime) of reaction intermediates. With ^{12}CO and ^{13}CO exhibiting essentially identical reactivity, the steady-state of the system is essentially not affected by the isotopic switch. Key findings are: (1) converages in intermediates are not controlled by surface-blocking side products, but rather by intrinsic kinetic and surface properties; and (2) activity decline upon aging is driven by changes in catalytic properties of the surface rather than by surface blocking. Both statements pertain to nickel-derived catalysis in a specific operation window.

319. *Studies of Supported Metal Catalysts*

D.M. Hercules **$89,782**
Department of Chemistry

We have examined two series of hydrodesulfurization (HDS) catalysts that consist of various cobalt or nickel loadings (1 9.5 wt%) on 10 wt% MoO_3TiO_2. Thus, the role of the promoter (nickel or cobalt) and the influence of changing the support (TiO_2 versus γ Al_2O_3) has been assessed. The catalysts were characterized in their oxidic, reduced, and sulfided state by ESCA, ISS, LRS, and XRD. We have investigated the influence of additives (e.g., boron) known to promote HDS reaction. The effect of boron on the state and dispersion of $Mo-Al_2O_3$ and $Co-Al_2O_3$ catalysts was examined. Quantitative determination of various species present was accomplished by ESCA analyses of the oxidic, reduced, and sulfided catalysts. A method employing LRS was developed for accurate and easy quantification of phases commonly found in commercial HDS catalysts. The method is based on the use of internal standard, and allows quantitative measurement of phases that cannot be readily quantified by other analytical techniques. The method has been successfully applied for the determination of MoO_3 present in $NiMo-Al_2O_3$ catalysts.

320. *Infrared Studies of Influence of Alkali Metals on C-O Bond in Chemisorbed Carbon Monoxide*

J.T. Yates **$271,700**
Department of Chemistry **(24 mo.)**

This research project is designed to probe the interaction of adsorbed alkali metals and electronegative poisons with adsorbed carbon monoxide on transition metal single crystal surfaces. Information obtained by reflection infrared spectroscopy, x-ray, photoelectron spectroscopy, and temperature programmed desorption will yield models of the interaction, and deeper understanding of the alkali promotion effects and electronegative poisoning effects observed in catalytic chemistry on transition metals. Recently, the range of S poisoning on a nickel(111) single crystal has been determined.

Purdue University
West Lafayette, Indiana 47907

321. *Reduction of Aromatic Compounds Derived from Coal by Calcium*

R.A. Benkeser **$65,000**
Department of Chemistry

The versatility of the new calcium reducing system has been elaborated further by reducing aromatic compounds like naphthalene, tetralin, anthracene, and anisole under Birch conditions. Naphthalene is reduced in good yield by calcium in a mixture of n-butylamine, ethylenediamine, and t-butyl alcohol to 1, 4, 5, 8-tetrahydronaphthalene. Tetralin is reduced in a similar fashion to 1, 2, 3, 4, 5, 8-hexahydronaphthalene. Anthracene is reduced to 1, 4, 5, 8, 9, 10-hexahydroanthracene and anisone to 2, 5-dihydroanisole. All of these reductions are more selective when carried out at 0°C than at ambient temperatures. Pure ethylenediamine freezes at about 9°C, hence the presence of a second amine (n-butylamine in the above cases) provides a solvent mixture that remains fluid at 0°C. A wide variety of other additives can be used to achieve this anti-freeze effect. In all the solvent mixtures used, the presence of ethylenediamine was essential. Only in pure methylamine did calcium reductions proceed at all, but the product disribution was very complex. The calcium-mixed amine system was used successfully to reduce an SRC-II-coal-derived liquid to probe for sulfur-containing polynuclear aromatic hydrocarbons. Using tandem mass spectrometry as an analytical tool, the presence of o-cyclohexylthiophenol and o-ethylthiophenol in the reduced sample was established unequivocally.

Rensselaer Polytechnic Institute
Troy, New York 12180

322. *Homogeneous Carbon Monoxide Fixation*

A.R. Cutler **$100,000**
Department of Chemistry

$Cp(CO)_3Mo^+$ (i.e., Mp^+ reacts with $Cp(CO)(L)FeCH_3$ (L=CO, PPh_3) either as a Lewis acid (L=CO: giving $FpC(CH_3)OMp$) or as an oxidizing agent (L=PPh_3: giving $MpCH_3$). This latter chemistry parallels that when Mp· (via MpH–Ph_3C·) reacts with organo Fe–CH_3^+ complexes, although Fe–$COCH_3^+$ complexes (17-electron) and Mp· afford $FeC(CH_3)OMp$ systems. These arguments are supported by results of electrochemical studies. Other organometallic Lewis acids studied include $(CO)_5M^+$(Mn,Re), $Cp(CO)(L)Fe^+$, Cp_2WCl^+, and $Cp(CO)(NO)Re^+$. The reductive chemistry of μ-(η^1-C,O) acetyl complexes M–$C(CH_3)O$–M [M=Cp(CO)(L)Fe, Mp, Wp, Cp(CO)(NO)Re] also has been investigated. Attempts at preparing heterobimetallic μ-(η^2–C,O) acetyl complexes $Cp(CO)_2Mo(COCH_3)M^+$ [with M=Cp(CO)Fe, CpNi, and $Mn(CO)_4$] have so far proved unsuccessful. In these studies, doubly unsaturated Lewis acids $CpNi^+$, and so forth were reacted with $MpCH_3$. Selective conversion of two CO's on $CpFe(CO)_3^+$ to ROCHCHO and three CO's to malonic ester $CH_2(CO_2R)_2$ has been accomplished. The former entailed isomerizing $FpCH(OR)CH_2OR^+$ to $Fp(RCH{=}CHOR)^+$, then hydrolysis to FpCH(OR)CHO; the latter required alkoxycarbonylation of $FpCH_2CO_2R$. A carbonylation study of $Cp(CO)_2FeCH_2R$ complexes [in which Cp was replaced by η^5-indenyl or $C_5(CH_3)_5$, iron by ruthenium, CO by PPh_3 and $P(OMe)_3$, and R=H, CH_3, OMe, Ph, CO_2Me] provided conditions for generating iron acyl complexes under mild conditions.

University of Rochester
Rochester, New York 14627

323. *Transition Metal Activation and Functionalization of Carbon Hydrogen Bonds*

W.D. Jones **$72,982**
Department of Chemistry

This project focuses on the activation and cleavage of carbon-hydrogen bonds by homogeneous transition metal compounds. Our initial work has been directed towards understanding the kinetic vs. thermodynamic differences between alkane and arene activation by the reactive intermediate $[(C_5Me_5)Rh(PMe_3)]$. We have found a tremendous thermodynamic preference for arene activation, whereas the kinetic preference of the intermediate is extremely small. Other studies involve the mechanism and thermodynamics of intra- and intermolecular alkane and arene C–H bond activation in the series of complexes $(C_5Me_5)Rh(PMe_2R)(R)(H)$. For R= propyl or benzyl there is little kinetic selectivity for intra- vs. intermolecular activation of arenes or alkanes, although there is a large thermodynamic selectivity favoring intramolecular activation. Temperature-dependent rate studies indicate that differences in the entropy of activation between intra- and intermolecular reaction are not important in this system.

University of South Carolina
Columbia, South Carolina 29208

324. *Studies of the Hydrogenation of Small Unsaturated Molecules Using Organometallic Cluster Compounds as Catalysts*

R.D. Adams **$86,000**
Department of Chemistry

Polynuclear transition metal (cluster) compounds are being investigated for their ability: (1) to activate hydrogen and unsaturated small molecules (e.g., CO, CO_2, alkynes, alkenes, and related heteronuclear molecules); (2) to induce bonding rearrangements in ligands; and (3) to produce hydrogen addition to unsaturated ligands. The products of reaction sequences are isolated and characterized by infrared, NMR, and single-crystal x-ray diffraction methods. The importance of polynuclear coordination in ligand transformations is studied. It is hoped that the reaction sequences can be converted into useful catalytic cycles.

SRI International
Menlo Park, California 94025

325. *High Temperature Chemistry of Complex Vaporization-Decomposition Processes*

D.L. Hildenbrand, R.D. Brittain, **$65,000**
K.H. Lau
Physical Sciences Division

The project objective is to obtain fundamental thermodynamic data for a variety of high-temperature vaporization-decomposition processes that are relevant to current and emerging energy technologies such as stack gas cleanup, coal gasification, hydrogen generation, and MHD. These processes are being studied by high-temperature mass spectrometry and the torsion-effusion method so that both vapor composition and absolute pressures are determined. For substances that simultaneously undergo both decomposition and direct vaporization, particular emphasis is on quantitative determination of the relative contributions from each process, and on thermochemical characterization of the complex vapor species. Current studies are concerned primarily with metal sulfate and carbonate processes, with recent work on the sulfates of lithium, nickel, and cobalt. The effects of certain additives that catalyze sulfate decomposition are also being studied, since kinetic and mechanistic features have a crucial bearing on the interpretation of the dynamic effusion measurements, as well as on the technological applications of these processes.

326. *Adsorption Thermodynamics and Surface Transport of Metal Catalysts Poisons*

H. Wise **$80,500**
Materials Research Laboratory

This research seeks to understand the binding energy of sulfur and halogen adatoms to metal surfaces in order to relate catalyst poisoning and reactivation to covalent bond formation. The experimental measurements involve studies of equilibrium adsorption and surface diffusion on single crystals of different orientations and on highly dispersed metal catalysts. The techniques employed include classical studies of reversible adsorption at low surface coverages, temperature-programmed desorption and surface reaction, Auger electron spectroscopy for diffusional transport, low-energy electron diffraction for determination of surface coordination and reconstruction, and segregation experiments for study of the interaction of different co-adsorbed surface species. At low surface coverage of sulfur significant variations in binding energy have been observed for different metals. Relative to nickel the sulfur adatoms are less strongly bound in the series, Ni > Co > Ru > Fe > Ir > Cu > Pt. Typically the bonding of sulfur appears to involve the sp and d bands of the metals and the sulfur 3p orbitals, as observed by photoelectron spectroscopy. Theoretical correlations are in progress to relate the binding energy of sulfur to the electronic structure of the metal.

Stanford University
Stanford, California 94305

327. Catalytic Steam Gasification of Carbon
M. Boudart **$80,863**
Department of Chemical Engineering

Platinum samples supported on alumina are currently being investigated as model systems by means of infrared adsorption spectroscopy. Adsorption of CO is used as a surface probe to determine the accessible metal surface. Samples of $Pt\text{-}Al_2O_3$ containing carbonaceous species show that the majority of the platinum surface is not covered with strongly bound coke or graphitic carbon. Current evidence suggests the coke is located on the Al_2O_3 support near the platinum sites. In another project, molybdenum carbide was investigated as a new catalyst for the gasification of carbon by dihydrogen. These studies show that at equal metal amount, molybdenum carbide is only slightly less active than platinum. This makes this carbide one of the most active catalysts for this reaction. In addition, x-ray absorption spectroscopy studies on both the platinum-carbon and MoC_x-carbon catalysts suggest that the metal atoms in both systems form bonds with carbon atoms of the support, as postulated in our earlier studies of metal catalyzed gasification of carbon.

328. Molecular Beam Studies of the Dynamics and Kinetics of Heterogeneous Reactions on Single Crystal Surfaces
R.J. Madix **$110,000**
Department of Chemical Engineering

The dynamics of the activated adsorption of CO_2 and H_2 on nickel(100) were studied. Both reactions are important elements in the hydrogenation of CO_2 to methane and higher hydrocarbons as well as the water gas shift reaction. With increasing translational energy from 2 to 25 kcal/gmol the probability of dissociation of $CO_{2(g)}$ to adsorbed CO and atomic oxygen on the clean surface increased from 7×10^{-4} to 10^{-1}. An increase to 0.3 was achieved by populating low-lying vibrational states. The lobular angular distribution of the scattered, unreacted CO_2 species indicated that scattering was direct and not dominated by trapping. Preliminary measurements of the average velocity of scattered CO_2 indicates transfer of translational to internal energy upon collision with the surface. Dissociation of dihydrogen was found to be translationally activated as well, though the low energy limit was 0.2, increasing to 0.8 at 2.5 kcal/gmol incident energy. The weak dependence of the dissociation probability with kinetic energy was accounted for by quantum mechanical tunneling using an asymmetric Ekart potential. The isotope effect for D_2 was in the direction predicted. Developments in the apparatus made during this grant period facilitate wider control and measurement of the dynamic variables, including incident and reflected velocities and scattering distributions.

Syracuse University
Syracuse, New York 13210

329. Metal-Support Interactions: The Effect of Catalyst Preparation on Catalytic Activity
J.A. Schwarz **$75,600**
Department of Chemical Engineering and Material Sciences

A scientific basis for design and control of catalyst systems can be developed by examining the relationship between catalyst preparation procedures and the activity, selectivity, and stability of the finished catalyst. In our studies, the master variable for preparation of catalysts is the pH of the solution. Nickel catalysts dispersed on a γ-alumina carrier were prepared using reagent grade $NiNO_3$ and different preparation conditions. The following techniques were employed to characterize each of the catalysts: (1) temperature-programmed desorption (TPD); (2) temperature-programmed reaction (TPR); (3) steady-state kinetics; and (4) temperature-programmed surface reaction (TPSR). The methane peak temperatures during TPR vary for each of the catalysts and clearly indicate that at least three forms of nickel can be present on Al_2O_3. The effects are dependent on the nickel weight loading and the pH of the impregnating solution. Steady-state kinetics were measured from 430 to 530 K in a 3 to 1 H_2-CO mixture by incrementally increasing the temperature without intermediate reduction. The Arrhenius plots of the steady-state rates show an activation energy dependent on pH. After these kinetic studies, the catalyst was cooled to room temperature in helium and TPR spectra of the carbon residue deposited during reaction were obtained. The carbon inventory is a function of the nickel weight loading and the pH of the impregnating solution. At least five forms of carbon are deposited on the catalyst surface during steady-state reaction.

University of Texas
Austin, Texas 78712

330. Study of Synthesis Gas Conversion Over Metal Oxides
J.G. Ekerdt **$57,486**
Department of Chemical Engineering

The goals of this project are (1) identification of the reaction intermediates present during CO hydrogenation reactions, (2) determination of the reaction pathways whereby the intermediates are converted into products, and (3) the development of an understanding of the causes for catalytic activity and selectivity. Direct CO hydrogenation into branched alkanes, isosynthesis, is being investigated over zirconium dioxide and alkali-promoted zirconium dioxide. High-pressure (35 atm) rate studies are performed to examine the primary products and establish the kinetics of C_1 to C_4 isosynthesis product formation. Atmospheric-pressure studies are performed to determine the catalytic reactions between CO, CO_2, H_2, and the zirconium dioxide surface and to gain insight into the reactions that initiate isosynthesis. The results from both pressure regimes are being used to develop a mechanism for the production of low-weight alcohols and for isosynthesis. The mechanism will be used as the basis for designing experiments directed toward the causes for metal oxide activity and selectivity.

Texas A and M University
College Station, Texas 77843-3255

331. Catalysts and Mechanisms in Synthesis Reactions

J.H. Lunsford **$84,599**
Department of Chemistry

This project seeks to understand the support and promoter effects that influence the catalytic properties of supported metals (e.g., palladium) for the formation of alcohols. Controlled modification of palladium supported on silica, for example by the addition of lithium ions, can transform an inactive catalyst into one that rivals commercial catalysts for methanol synthesis activity. Pure palladium is relatively inactive, thus the support plays an essential role perhaps by stabilizing intermediate species. Infrared experiments are underway to detect these intermediates if they exist. Another aspect of the research involves a study of matrix-isolated gas phase radicals that are produced on surfaces of catalytic importance. Recent work on lithium-promoted magnesium oxide shows that $[Li^+O^-]$ centers are active in the generation of methyl radicals. These centers are present on oxygen-rich surfaces, which is surprising since magnesium oxide normally is considered to be a nonreducible oxide. Radical formation has been compared over bismuth oxide, bismuth-molybdate, lead oxide, magnesium oxide, and lithium-promoted magnesium oxide with methane, ethane, ethylene, and propylene as the reactants. All of the oxides were capable of generating alkyl radicals from propylene, which has the smallest C–H bond strength, but only MgO and Li-MgO were capable of generating alkyl radicals from alkanes.

332. Properties of Lanthanide Oxides as Supports for Transition Metal Catalysts

M.P. Rosynek **$78,700**
Department of Chemistry

This research project involves a systematic investigation of the influence exerted by selected lanthanide oxide supports, principally those of lanthanum, cerium, praseodymium, and europium, on the catalytic behaviors of both well-dispersed (platinum, rhodium) and poorly-dispersed (iron, cobalt, nickel) transition metals, with a view toward identifying evidence for significant metal–support interactions. Supports being studied as a basis of comparison include silica, alumina, and titania. Catalytic behaviors of the various metals are being evaluated for appropriate diagnostic reactions (CO hydrogenation and paraffin hydrogenolysis-dehydrocyclization) as a function of reaction conditions and support identity. These results are being correlated with those of accompanying characterization studies, involving infrared and x-ray photoelectron spectroscopies and selective chemisorption measurements, in an attempt to elucidate the nature and extent of support-induced modifications of catalytic behaviors.

University of Utah
Salt Lake City, Utah 84112-1183

333. Ligand Intermediates in Metal Catalyzed CO Reduction

J.A. Gladysz **$96,768**
Department of Chemistry

The project objective is the synthesis and study of homogeneous complexes containing ligand types (–CHO, =CHOH, –CH_2OH, ≡C, ≡CH, =CH_2, $H_2C=O$, –OCHO, CO_2, and so forth) believed to be intermediate in the metal catalyzed conversion of $CO–H_2$ and CO_2H_2 gas mixtures to organic molecules. We seek mechanistic understanding of the steps involved in catalytic CO and CO_2 reduction and insight needed for the design of new catalysts. We are currently studying the synthesis and reactivity of α-hydroxyalkyl complexes $L_nMCH(R)OH$. The first isolable complex of this type to undergo carbonylation (to an acyl complex $L_nMCOCH(R)OH$) has been discovered, and the mechanism is under investigation. Sequential treatment of formyl complex $(\eta^5\text{-}C_5H_5)$ Re–(NO)(PPh_3)(CHO) with LDA and then $CH_3OSO_2CF_3$ gives $(\eta^5\text{-}C_5H_4CHO)$ Re (NO) (PPh_3)–(CH_3)–the first carbon–carbon bond forming reaction of an η^1-formyl ligand. Metal hydrides are also key intermediates in catalytic CO and CO_2 chemistry. We find that the reaction of hydride complex $(\eta^5\text{-}C_5H_5)$ Re (NO) (PPh_3) (H) with n-BuLi–TMEDA to give Li^+ $[(\eta^5\text{-}C_5H_5)$ Re (NO) $(PPh_3)]^-$ proceeds via $(\eta^5\text{-}C_5H_4Li)$–Re (NO) (PPh_3) (H)–a new ligand assisted metal hydride deprotopation mechanism.

334. Liquid and Solid ^{13}C Magnetic Resonance Study of Hydrocarbons and Related Substances

D.M. Grant, R.J. Pugmire **$99,800**
Department of Chemistry

We recently finished our work on hydroaromatic model compounds, which showed a correlation between conformation and chemical shifts. Work on solid state nuclear magnetic resonance (NMR) methods of single crystal and magic angle spinning (MAS) involves model compounds to be used for calibration and standardization of spectra of coals, coal macerals, and so forth. Current work on single crystals provides a better understanding of shielding anisotropies and the orientational features of the important dipolar dephasing experiment. Rotating a single crystal gives data on chemical shift anisotropy; initial results show relaxation anisotropy can be studied. Both the dipolar dephasing rate and relaxation anisotropy depend on the orientation of C–H bonds. The single crystal work provides basic information on these processes. An ultra high speed (0 to 8,000 r.p.s.) rotor for MAS work has been developed. The higher rotation rates allows use of our 4.7 tesla magnet instead of the 2.35 tesla systems used previously. Reduced rotor diameters also allow for significant increases in the RF fields at reduced power dissipation and improved cross polarization (CP) efficiencies. Work on the molecular dynamics of benzyl alcohol and pentanol adsorbed on zeolites using CP/MAS methods contributes information on catalytic processes.

335. Comprehensive Characterization Studies of Sulfided Molybdena Catalysts

F.E. Massoth **$74,000**
Department of Fuels Engineering

The goal of the present work is to characterize a wide variety of supported molybdena sulfide catalysts with a number of different characterization techniques, and determine their catalytic activities for model compounds representative of several functionalities present on these catalysts in order to relate catalytic activities to catalyst properties (viz., structure, dispersion, active sites) of the active phase. Several newer techniques not available or not employed in earlier studies, as well as some conventional ones, will be used to characterize the catalysts. These include chemisorption of selected gases, active OH content of the supports, $H_2{}^{35}S$ exchange, electron spectroscopy for chemical analysis, x-ray diffraction, and SH content. A number of catalysts containing 4 or 8% molybdenum on different aluminas, prepared by impregnation at various pH's, have been found to have widely different hydrodesulfurization activities. Detailed characterization of these catalysts is in progress.

Wayne State University
Detroit, Michigan 48202

336. Synthesis, Static, and Reactive Characterization of Supported Organometallics
A. Brenner **$85,000**
Department of Chemistry

Temperature-programmed decomposition (TPDE) of carbonyls on a variety of supports has been examined. Magnesia is similar to alumina in its ability to stabilize subcarbonyl species, but TiO_2 does not. For zeolites, stabilization is enhanced with decreasing silicon-aluminum ratio. TPDE can be used to prepare well dispersed and low-valent catalysts of many transition metals. These properties often enhance catalytic activity. Photolytic activation at ambient temperature has also been used to avoid thermal sintering. The extent of decarbonylation is a function of many variables. Nearly complete photolysis is achieved using silica or an hydroxylated alumina as a support. Using hydrogen as a sweep gas during photolysis results in some of the carbonyl ligands being converted to methane. Photolyzing $Mo(CO)_6$ results in a catalyst which appears to be nearly 100% dispersed and is extremely active for hydrogenation. The hydrogenation of benzene has been investigated over both salt and carbonyl catalysts, to yield the first extensive ordering of activities for this model reaction. After reduction at 600°C, eight of the carbonyl derived catalysts are more active than salt-derived catalysts. With the exception of ruthenium, the enhancements are confined to base metals since these are difficult to reduce when prepared from salts. Salts have also been reduced at 1000°C to encourage generation of low-valent material. Four catalysts of base metals show improved activity after high-temperature reduction.

University of Wisconsin
Madison, Wisconsin 53706

337. Mechanistic Studies Related to the Metal Catalyzed Hydrogenation of Carbon Monoxide to Hydrocarbons
C.P. Casey **$108,000**
Department of Chemistry

The synthesis of organometallic compounds that contain functional groups similar to those proposed in homogeneous and heterogeneous catalyzed carbon monoxide reduction is being carried out, so that the properties and reactions of these species can be studied. This basic information should contribute to the understanding and eventual design of catalysts for the reduction of carbon monoxide. Detailed studies of the synthesis and reactions of metal formyl compounds (M-CO-H) and hydroxymethyl metal compounds (MCH_2OH) (models for intermediates in the homogeneous hydrogenation of CO) are being carried out. Compounds with CH_3, CH_2, and CH groups bridging between two iron atoms have been synthesized as models for intermediates in the heterogeneous catalysis of CO hydrogenation. Carbon-carbon bond forming reactions of the CH compounds with alkenes and with CO are being explored. Several heterobimetallic compounds linked by a heterodifunctional ligand have been synthesized. Their reaction with hydrogen is being studied as a possible route to heterobimetallic dihydrides that might serve as catalysts for CO reduction. New compounds with directly bonded early and late transition metals have been synthesized and their fundamental chemistry is being explored; for example, $(C_5H_5)_2Zr[Ru(CO)_2C_5H_5]_2$ has been made and its reactions with CO and H_2 are under investigation.

338. Acid Sites Formed by Doping Cations onto Oxide Surfaces: Theoretical Aspects and Experimental Studies
J.A. Dumesic **$63,300**
Department of Chemical Engineering

During the past year our research on the acidic properties of mixed metal oxides has focused on silica-supported iron samples. Moessbauer spectroscopy studies showed that iron interacts strongly with the silica support, leading to a surface phase which is not readily reducible to metallic iron. Pyridine adsorption measurements indicated that acid sites are generated by incorporation of iron into the silica surface. Infrared spectra of the adsorbed pyridine showed that these new sites are Lewis acids, and Moessbauer spectroscopy confirmed that these acid sites are associated with coordinatively unsaturated iron cations. The effect of the iron oxidation state in determining the strength of these acid sites was probed by monitoring the desorption of pyridine at elevated temperatures from samples pretreated to vary the relative amounts of ferric and ferrous cations. In general, ferric cations on silica generate stronger Lewis sites than ferrous cations. This conclusion was also reached by comparing the positions of the infrared bands of pyridine adsorbed on the various samples; that is, the band near 1600 cm^{-1} was shifted to higher wavenumbers on the stronger Lewis acid sites. We are currently extending these studies to iron on other oxide supports.

Yale University
New Haven, Connecticut 06511

339. Studies in Carbon-Carbon Bond Activation
R.H. Crabtree **$94,500**
Department of Chemistry

The aim of this research is to find ways of cleaving carbon-carbon bonds in alkanes and other related hydrocarbons with transition metal complexes. We believe that to do this we first have to break carbon-hydrogen bonds to give an organometallic species that can subsequently undergo a carbon-carbon bond cleavage. For example, we had shown that cyclopentanes can be dehydrogenated to cyclopentadienyl complexes by $[IrH_2(solv)_2L_2]$ cations. We have now shown that a similar reaction with *gem-dimethylcyclopentane* gives a dimethylcyclopentadiene complex. This undergoes alkyl transfer to give a methyl iridium cyclopentadienyl complex. This is the first case of homogeneous carbon–carbon bond cleavage in alkanes by a metal complex. Initial studies suggest that a second mechanism is operating which might be applicable to alkanes in general. We feel that we may be close to having a homogeneous reforming catalyst.

340. Selectivity, Activity, and Metal–Support Interactions of Rhodium Bimetallic Catalysts

G.L. Haller **$84,800**
Department of Chemical Engineering

Three bimetallic systems have been studied: Rh–Pt, Ru–Cu, and Rh–Ag. In all three systems our goal has been the determination of the effect of the support on the kind and degree of metal–metal interaction. Small particles of Rh–Pt are found to be enriched on rhodium on all supports, the degree of enrichment increasing in the order $SiO_2 < Al_2O_3 < TiO_2$. The kind of SiO_2 used to support Ru–Cu is found to have a large influence on the change in the H/Ru ratio when ruthenium and Ru–Cu–SiO_2 catalysts are compared, although the effect on ethane hydrogenolysis is comparable. For pure rhodium supported on TiO_2 and reduced at high temperature, extended x-ray absorption fine structure (EXAFS) analysis suggests direct Rh–Ti bonding following a high temperature reduction. EXAFS also indicates that there is a stronger interaction between silver and TiO_2 than silver and SiO_2 and clearly demonstrates that there is greater metal–metal interaction for Rh–Ag supported on TiO_2 than for Rh–Ag supported on SiO_2.

341. The Role of d-Electrons in Chemisorption and Metal Support Interactions Studies by Electron Spectroscopy

V.E. Henrich **$69,500**
Section of Applied Physics

This research project uses model-supported catalysts (i.e., small amounts of rhodium deposited *in situ* (UHV) onto well characterized single-crystal rutile titanium dioxide surfaces) and surface-sensitive electron spectroscopies (including photoemission and Auger spectroscopy) to examine the role of d-electrons, support-electronic structure, and geometric effects in strong metal–support interactions (SMSI). Simultaneously, an attempt at determining the morphology of the metal particles by using transmission electron microscopy (TEM) is being made by substituting TEM grids on which a polycrystalline TiO_2 layer has been grown for the monocrystalline substrate mentioned above. As we previously observed, heating the model catalyst to 400°C leads to a partial covering of the metal by an oxide of titanium. This oxide migration is intimately linked to the SMSI behavior exhibited by the Rh–TiO_2 system. Experimental results currently being obtained on even more perfectly stoichiometric substrate surfaces should lead to a clarification of the role played by surface defects in promoting metal–support interactions as well as a differentiation between annealing in UHV or in an H_2 atmosphere.

342. Energies of Organic Compounds

K.B. Wiberg **$97,000**
Department of Chemistry

This research project is designed to provide information on the energies of organic compounds via reaction calorimetry and theoretical calculations, and to use these data to improve empirical and semi-empirical schemes for estimating the energies of these compounds. Heats of vaporization are being measured so that the thermochemical data may be corrected to the vapor phase. The data are also being used to explore steric effects and other structural effects on energies. Reactions being studied include the hydration of alkenes, hydrolysis of ketals, reduction of ketones, and rearrangements of small ring hydrocarbons. Theoretical calculations are being used to estimate the energies of interesting compounds, which have not as yet been prepared, and to study the intramolecular interactions (force constants and rotational barriers) and charge distributions that are used in molecular mechanics.

Separation and Analysis

Aerospace Corporation
Los Angeles, California 90009

343. Isotopically Selective, Two-Step, Laser Photodissociation of Molecules

P.F. Zittel **$121,000**
Chemistry and Physics Laboratory

This research project is directed toward understanding those photophysical, energy transfer, and chemical processes relevant to isotope separation by two-step laser photodissociation of small molecules. The two-step technique involves the excitation of molecules containing a chosen atomic isotope to an excited vibrational state by an infrared laser, followed by ultraviolet laser photodissociation and scavenging of the photofragments. Infrared laser absorption measurements and mass spectrometric analysis of the photoproducts reveal the effect of vibrational excitation on the photodissociation cross section, and give the isotope enrichments. Of particular interest are measurements of vibrationally state-specific photodissociation cross sections for different vibrational modes of a molecule. Two-step photodissociation of OCS has led to the separation of all stable isotopes of oxygen, carbon, and sulfur, and to a determination of the 249 nm photodissociation cross section of the ν_1 and $2\nu_2$ vibrational states of OCS. Rate constants for various vibrational energy transfer processes and chemical reactions may also be inferred from isotope enrichment measurements. Previous work on gas phase, room temperature samples is being extended to cryogenic solutions.

University of Arizona
Tucson, Arizona 85721

344. Chelating Extractants of Improved Selectivity

H. Freiser **$80,000**
Department of Chemistry

This research is designed to develop chelating extractants of improved selectivity for separating individual lanthanide and actinide ions. Emphasis is on uncovering molecular structural parameters of importance in the design of such extractants. Use of pattern recognition techniques represents one approach to the elucidation of molecular parameters. Study of the extraction equilibria for representative tervalent lanthanides with selected members of chelating extractants of the N-acylphenylhydroxylamine, 8-quinolinol, acylpyrazolone, and other families is being used, both because they include some likely candidate extractants and because present gaps in fundamental data required to apply pattern recognition are thereby being eliminated.

Auburn University
Auburn, Alabama 36849

345. Interfacial Chemistry in Solvent Extraction Systems

R.D. Neuman **$105,000**
Department of Chemical Engineering

The objective of our research is better understanding of the complex chemistry involved in the solvent extraction of metal ions by combining interfacial studies with mass transfer, interfacial turbulence, and coalescence studies on a relatively simple, but well-characterized, solvent extraction system. Interfacial tension measurements provided evidence that aggregates (possibly reversed micelles) exist above a critical HDEHP concentration, and their formation corresponds to significant increases in both the amount of metal extracted and the rate of metal extraction for the system HDEHP–n-hexane–$CaCl_2$ solution. Our studies are being extended to more complex systems of immediate, practical relevance such as the extraction of Co^{2+}, Ni^{2+}, Zn^{2+}, and $UO_2{}^{2+}$. The effects of the various metal ions and their concentration, acidity, extractant concentration, media (chloride, nitrate, sulfate), extractant type (HDEHP, PC 88A, CYANEX 272), as well as diluent type (n-hexane and xylene) and organic phase modifiers (isodecanol and TBP), on reversed micelle formation, metal distribution equilibria, and extraction kinetics are being studied to determine whether correlations exist between interfacial properties (interfacial tension, interfacial elasticity, interfacial viscosity) and mass transfer. The nature, size, and size distribution of the aggregates in organic diluents will be investigated in greater detail using a variety of techniques.

Bend Research, Inc.
Bend, Oregon 97701-8599

346. Fundamentals of Coupled-Transport Membranes

D. Friesen **$93,900**
Division of Membrane Separation

The project objective is to study the fundamentals of coupled-transport membranes as applied to the concentration and separation of uranium and other metals. Coupled-transport membranes consist of a water-immiscible, liquid complexing agent held by capillary forces in the pores of a microporous polymeric support. This membrane separates two aqueous solutions of unequal concentrations. The complexing agent can pick up ions on one side of the membrane and carry them across the membrane by diffusion in the form of a neutral complex. Metal ions can be transported from a dilute to a concentrated solution by coupling their flow to that of another ionic species. The membranes are also selective due to the selectivity of the complexing agent toward one metal ion over other similar metal ions. Thus, coupled transport is of potentially practical value in hydrometallurgy and in the treatment of radioactive wastes. Current efforts focus on studying and improving the long-term performance of coupled-transport membranes. A model that is consistent with observed membrane performance has been developed. Based on this model, substantial progress has been made in developing membranes with commercially practical lifetimes.

Brigham Young University
Provo, Utah 84602

347. Separation of Selected Cations by Liquid Membranes

J.J. Christensen **$96,200**
Department of Chemical Engineering

Macrocycle-mediated cation transport using bulk, emulsion, and lipid vesicle liquid membrane systems is being investigated and modeled. In water–halocarbon–water bulk liquid membranes, coupled proton–alkali metal ion transport is being studied using proton ionizable macrocycle carriers. The relative fluxes of cations from cation mixtures in water–toluene–water emulsion membrane systems is under investigation using various macrocyclic carriers in the toluene phase, and various complexing anions in the interior receiving phase. The transport in these emulsion systems of metals as anionic species coupled to a pH gradient across the membrane is also being studied. Dicyclohexano-18-crown-6 and other macrocycles have been incorporated into phospholipid vesicles as a means of making the vesicles selectively permeable to cations. The chemical and thermodynamic characteristics of the interaction, individually and as mixtures, of Pb^{+2}, Ca^{+2}, Sr^{+2}, and Ba^{+2} with these vesicles is being investigated.

Brown University
Providence, Rhode Island 02912

348. Photochemical Generation of the Optoacoustic Effect

G.J. Diebold **$65,000**
Department of Chemistry

We conduct experiments to show that the chemically amplified optoacoustic effect can be used as a method of analysis for determining the mechanism of photochemical reactions in the gas phase (i.e., short wavelength light is used to initiate reactions in a spectrophone cell, and phase and amplitude of the resulting acoustic wave is measured). Since the heat release in the cell is governed by the secondary reactions initiated by the production of radicals, the acoustic signal acts as a measure of the rate of reaction. Experiments will be carried out to determine chain lengths directly using the optoacoustic effect. An inverse optoacoustic effect has been observed in this laboratory. Experiments are conducted to determine the origin of the effect and to characterize its properties with respect to several parameters. Chemi-ionization detection also will be investigated. A specific, highly sensitive detection scheme based on chemi-ionization is proposed for use in gas chromatography. The energetics of some ionization reactions will be studied with regard to the suitability of the reactions for the detector and to determine thermodynamic information about the reactions themselves.

University of California
Irvine, California 92717

349. *Studies of Isotopic Mass Effects in Chemistry*
M. Wolfsberg **$80,000**
Department of Chemistry

This project entails theoretical studies of isotopic mass effects on molecular properties. Statistical mechanical calculations of isotope effects on a variety of molecular properties require a knowledge of rotational-vibrational energies of molecules and of isotope effects on these energies. Such energies are being calculated by the variational method for formaldehyde, water, and other molecules. The tunneling phenomenon and isotope effects on tunneling are being studied by investigating the vibrational energy levels of molecules with double-minimum potentials, in particular ammonia. Molecular dynamics calculations are being carried out on aqueous solutions of rare gases and of diatomic molecules such as nitrogen, to elucidate isotope effects on Henry's law constants as well as to study the structure of these solutions. In this connection, a molecular dynamics study of energy transfer between rotationally and/or vibrationally hot diatomic molecules and water (modeled either as liquid water or as a water clathrate surrounding the diatomic moleule) is being conducted.

University of California
Los Angeles, California 90024

350. *Multiheteromacrocycles That Complex Metal Ions*
D.J. Cram **$125,000**
Department of Chemistry and Biochemistry

The general objectives of this research are to design, synthesize, and evaluate new types of cyclic and polycyclic organic ligand systems for their abilities to complex and lipophilize selectively guest metal ions. Correlations are sought between ligand structures and their binding free energies, their rates of complexation-decomplexation, and their solvation effects. Desired properties are high selectivity, rapid rates of complexation, and incorporation of detecting systems into the ligand. The principles of complementarity of host and guest and of host preorganization are being tested as guides in ligand design. Organized arrays of most of the functional groups of organic chemistry are being tested as ligating sites. Particular emphasis is placed on those systems that contain weakly basic nitrogen, sulfur in various oxidation states, and carbonyl groups of various types. Synthetic methods are being developed which lead to enforced preorganization of binding sites. Solvent effects on binding are being studied.

Calspan Advanced Technology Center
Buffalo, New York 14225

351. *Energy Transfer and Reaction Kinetics of Vibrationally Pumped Molecules*
J.W. Rich **$67,332**
Department of Physical Sciences

This is a project for experimental and analytical research into energy transfer and reaction kinetics of vibration-to-vibration (V-V) pumped molecules. Extreme V-V pumped vibrational population distributions in CO, NO, and other gaseous species are produced by optical excitation. Special emphasis is being placed on isotopic enrichment reactions of V-V pumped CO, which yield products enriched in ^{13}C, ^{17}O, and ^{18}O. Processes limiting vibrational up-pumping in CO and NO are being studied, especially vibration-to-electronic energy transfer from the pumped ground electronic state of these molecules to low lying excited electronic states. The rate equation kinetic modeling of these processes is being developed.

Columbia University
New York, New York 10027

352. *Utilization of Magnetic Effects as a Means of Isotope Enrichment*
N.J. Turro **$74,900**
Department of Chemistry

This research is aimed at developing novel methods for the separation of isotopes based on exploitation of differences in magnetic properties of isotopes. Emphasis has been placed on discovering reactions and conditions that allow the separation of isotopes that possess a finite magnetic moment from those that do not possess a magnetic moment. Successful systems have been designed for separation of ^{13}C (a magnetic isotope) from ^{12}C (a non-magnetic isotope), and for the separation of ^{17}O (a magnetic isotope) from ^{16}O and ^{18}O (non-magnetic isotopes). The restricted space provided by porous silica has proven to be an excellent environment for efficient separation of ^{13}C and ^{12}C based on the photolysis of dibenzyl ketone. The porous internal structure of zeolites is also an excellent environment for ^{13}C enrichment. The variation in zeolite structure offers a range of environments to serve for ^{13}C enrichment. Experiments are now in progress to determine how to optimize ^{13}C enrichment on zeolites.

George Washington University
Washington, District of Columbia 20052

353. *New High Temperature Plasmas and Sample Introduction Systems for Analytical Atomic Emission Spectrometry*
A. Montaser **$70,800**
Department of Chemistry

New high temperature plasmas and new sample introduction systems are developed for rapid elemental analysis of solutions and solids using atomic emission spectrometry. These devices offer promise of solving singularly difficult analytical problems that either now or are likely to arise in the future in the various fields of energy generation, environmental pollution, biomedicine, and nutrition. Emphasis is being placed on: (1) generation and fundamental investigation of annular helium inductively coupled plasmas that are suitable for the excitation of high energy spectral lines, with the intent of enhancing the detecting powers for a number of elements; (2) generation of plasmas that require low gas flows and low input power, with the intent of decreasing the cost of analytical determination; and (3) development and characterization of new sample introduction systems that consume microliter or microgram quantities of samples. Investigations include the fundamental principles behind the measurements, the evaluation of the analytical potentials of the devices developed, and the demonstration of the analytical methods in representative samples.

University of Georgia
Athens, Georgia 30602

354. *Fundamental Studies of Separation Processes*
L.B. Rogers **$65,500**
Department of Chemistry

There are three major areas of effort in this research. The first is concerned with the fundamental aspects of two different forms of liquid chromatography, adsorption, and steric exclusion, especially with respect to interaction during a given separation. Non-porphyrin compounds of vanadium and nickel, and commercial mixtures of oligomers of polystyrene are ideal solutes for these studies because each type of sample covers a wide range of molecular weights. The second area involves the identification of those non-porphyrin compounds using a variety of techniques. The third area is concerned with recycle chromatography, a promising approach to separations of isotopic species.

Georgia Institute of Technology
Atlanta, Georgia 30332

355. *Fundamental Studies with a Monodisperse Aerosol-Based Liquid Chromatography/Mass Spectrometry Interface (MAGIC-LC/MS)*
R.F. Browner **$80,000**
Department of Chemistry

An aerosol-based liquid chromatography/mass spectroscopy interface (MAGIC-LC/MS) has been constructed. This device uses monodisperse aerosol generation, atmospheric pressure desolvation and aerosol beam separation of solute particles and solvent vapor. The interface may be operated with equal ease on either magnetic sector or quadrupole instruments. The device is very simple to operate, and has minimal adjustments for setup. The interface may be connected to the mass spectrometer without modification to the instrument, and allows a complete choice of electron impact or chemical ionization modes. Recently, the aerosol beam separator has been redesigned, increasing the transport efficiency of the system and improving detection capability. Tests with a number of environmentally important compounds, such as carbamate and triazine pesticides and polynuclear aromatic compounds have given detection limits of approximately 10 ng.

University of Houston
Houston, Texas 77004

356. *Mechanisms of Cake Filtration*
F.M. Tiller, M. Tadros **$160,000**
Department of Chemical Engineering

The theory of particulate separation involving compressible, porous beds or sediments as found in sedimentation, filtration, centrifugation, and expression is being studied. The Darcy equation in either spatial or material coordinate form must be combined with a differential momentum balance to produce simultaneous equations involving the liquid pressure and the compressive effective pressure. Solution of these equations requires constitutive relations involving permeability, specific flow resistance, and porosity. Different boundary conditions, the presence of gravitational or centrifugal forces, and solid movement in sedimentation lead to different forms of the basic equation. This project aims at unifying the theory underlying the different types of solid-liquid separation and at developing techniques for determining empirical parameters involved in the constitutive equation. The structures of beds of dispersed and aggregated uniform, micron-sized particles are being related to compressibility. A rough predictive method for calculating parameters in functions relating porosity and permeability to effective pressure has been developed. Quantities used in the correlations include particle size and shape and degree of aggregation. An apparatus for simulating a continuous thickener by partially fluidizing a bed of fine particles has been constructed. Initial cake structure of deposits as affected by surface charge, suspension concentration, and agitation is being studied in relation to resistance to flow. Pressure distributions are used to study flow mechanisms and fine particle migration. The University of Houston and Martin Marietta Laboratories are cooperating in this research.

University of Illinois
Urbana, Illinois 61801

357. *Theta Pinch Discharges for Solids Vaporization and Elemental Chemical Analysis*
A. Scheeline **$66,000**
School of Chemical Sciences

A pulsed, magnetically constricted plasma (theta pinch) is being used for elemental chemical analysis. A 1.0 to 1.5 kJ discharge with rise time 2 μs is employed to heat and compress a plasma of either argon or helium. Various sample forms are being tested, as there is interaction between the shape of the sample, plasma formation, and plasma-sample interaction. Spatially-resolved spectra are being exploited to assist in resolving continuum and line background from analyte emission. Time resolution is also being performed. Our goal is to design a discharge system that can vaporize high melting solids (conducting or non-conducting) for matrix free determinations of elemental composition of the solids being studied. To date, only lower melting metals (e.g., brass and aluminum) have been successfully sampled. Because the plasma survives for only a few microseconds, only the surface of the sample is attacked by the discharge. Possibilities of controlling the depth of sampling and the area over which sampling occurs will be explored.

Kansas State University
Manhattan, Kansas 66506

358. *Development of a New Novel Hadamard Transform Infrared Spectrometer for Analytical Chemistry*
W.G. Fateley **$67,000**
Department of Chemistry

We will develop a special Hadamard infrared spectrometer to investigate the heterogeneous nature of substances such as coal samples. A newly designed Hadamard mask will facilitate this study. We will investigate the distribution of impurities, structural differences, material properties, and concentration variations in coals and silicon crystal wafers. This will be accomplished by the two-dimensional Hadamard fore mask accessory to the HTS spectrometer. The coals will serve as the source in an emission experiment and will be placed between the focusing optics and the two-dimensional Hadamard fore mask in a transmission experiment. Areas of variation that can be detected by infrared spectroscopy will provide new and important information about materials. The chemical variations with depth will be investigated in different coal samples. Using the photoacoustic detector and a Czerny-Turner monochromator equipped with an exit Hadamard mask, it will be possible to depth profile these coal samples. Using subtraction techniques developed in Fourier transform spectroscopy, it will be possible to examine the spectra of different depths and the chemical differences between the surface and the bulk of these coal samples. These investigations may be classified as two-dimensional depth spectroscopy.

Kent State University
Kent, Ohio 44242

359. Adsorption and Desorption of Hydrocarbons at Low Concentrations

R. Madey **$69,000**
Department of Physics

The aim of this research is to study the adsorption and diffusion of hydrocarbon gases through porous media adsorber beds. The approach involves calculations based on a mass-balance equation of the quantity of adsorbate adsorbed on an adsorbent, measurements of adsorption isotherms of hydrocarbons on activated carbon and polystyrene beads at selected temperatures, and studies of the dynamics of breakthrough curves with both a step-function and a pulse change of the input concentration. The breakthrough curves of binary mixtures exhibit interference phenomena where the output concentration of the weakly-adsorbed component increases above the input concentration until the other component elutes. An objective of this study is to provide an explanation of interference phenomena. The approach will be to obtain binary adsorption isotherms, to examine the mechanisms of intraparticle diffusion and longitudinal diffusion of the system, and to study the characteristics of the differential equation that governs the system.

University of Maryland
College Park, Maryland 20742

360. Study of Highly Selective Sorptive Effects with Applications to Paraffins and Petroporphyrin Separations

D.H. Freeman **$70,000**
Department of Chemistry

Organic biomarkers are of interest in areas that create a challenge to modern separation science. New sorptive materials and new uses of methodological principles are being studied. These efforts are focused on two goals. The rapidly achieved chemical selectivity of silicalite is being explored. This new sorbent, a zeolitic form of silica, is highly sorptive for the n-alkanes and their monomethylalkane isomers. Dimethylalkanes and other molecules of slightly larger cross sectional diameter are selectively excluded from silicalite. An improved analytical sequence is being developed to examine the methyl group positions in the monomethylalkanes. Such isolations from petroleum source materials may provide a possible indicator of geothermal stress. Similarly, the isolation of petroporphyrins is sought using selectivity multiplying sequences of short HPLC columns (1 to 3 cm length, 200 to 500 plates). This approach is an improvement over solid phase extraction. Several different petroporphyrin groups are isolated. Their tetrapyrrole ring structures are identified by their characteristic Soret band absorption of 400 to 410 nm light. Group sub-classification is based on interactions with a series of sorbents that are being screened for that purpose. A suite of characterized petroleum and shale oil samples will be examined.

University of Minnesota
Minneapolis, Minnesota 55455

361. Continuous Reaction Chromatography

R. Aris, R.W. Carr **$64,000**
Department of Chemical Engineering and Materials Science

Continuous reaction chromatography is a method for carrying out chemical reaction with simultaneous chromatography of reactants and products in a single continuous flow reactor. This can be accomplished by providing relative motion between the chromatographic packed bed and the feedstream. Investigations of the rotating cylindrical annulus for both liquid phase reaction-solid adsorbent and gas-solid catalytic reactions have been completed. A detailed modeling study of the behavior of a countercurrent moving bed chromatographic reactor has also been done. Experimental tests of a laboratory-scale countercurrent moving bed reactor are being carried out. Analysis of reaction products is being done by conventional gas chromatography and the performance of the reactor is being compared with theoretical predictions. The simulation of countercurrency by switching the feed between fixed columns is currently being investigated both theoretically and experimentally.

University of Missouri
Rolla, Missouri 65401

362. An Extraction/Separation Process with Extreme Energy Efficiency

S. Friberg, P. Neogi **$70,000**
Department of Chemistry

The purpose of this investigation is to examine the phase equilibria involved in an extraction/separation process with extremely low energy demand. The process uses the temperature dependent transitions of colloidal association structures in systems of water-polyethylene glycol, dodecyl ethers-aliphatic hydrocarbons to permit spontaneous extraction and separation with a temperature change of only 20°C. The main emphasis is placed on the role of liquid crystals to influence the kinetics of the extraction process.

National Bureau of Standards
Gaithersburg, Maryland 20899

363. Competitive Ion Kinetics in Direct Mass Spectrometric Organic Speciation

L.W. Sieck **$137,000**
Center for Chemical Physics

This research project involves the measurement of fundamental properties of gas phase ions, including fragmentation and reaction mechanisms and rates, structures, and the thermochemistry associated with ionization, protonation, and reaction. When appropriate, this information is then used to suggest chemical ionization techniques which incorporate competitive ion kinetics and permit identification and/or assay of specific compounds or classes of compounds occurring in complex organic mixtures. The experimental project uses the NBS pulsed high pressure mass spectrometer system as the prime facility; an ion cyclotron resonance instrument is also available. Work-in-progress includes determinations of enthalpies of protonation, hydration, and solvation of complex amines, ethers, and sulfur compounds, as well as systematic studies of the unimolecular kinetics associated with ion pyrolysis. Analogous measurements involving complex negative ions, particularly their thermal stability and reaction kinetics, are also currently receiving emphasis.

University of Oklahoma
Norman, Oklahoma 73019

364. *A Study of Micellar-Enhanced Ultrafiltration*
J.F. Scamehorn, S.D. Christian **$62,800**
School of Chemical Engineering and Materials Science

In micellar-enhanced ultrafiltration, surfactant is added to aqueous streams containing dissolved organics. Aggregates called micelles are formed, into which a very high fraction of the organic solute tends to be distributed. The solution is then passed through an ultrafiltration filter with pores just small enough to prevent the micelles from passing through. Cationic surfactants have been found to be superior to anionic or nonionic surfactants for this application. Phenolics and alcohols have been studied as sample solutes. The solute concentration present in the filtrate has been found to be equal to its unsolubilized concentration in the retentate and the surfactant concentration in the filtrate is slightly less than the mean ionic molality in the retentate. Therefore, micelles essentially are being completely rejected and the unsolubilized solute is in equilibrium across the membrane, while the surfactant monomer is being hindered as it transfers through the membrane. Solute rejections of as high as 99.7% with good fluxes and high recycle ratios have been observed, proving the feasibility of this new separation technique. In order to measure equilibrium properties in these solubilizing micellar solutions, a new analytical technique, semi-equilibrium dialysis, has been developed.

Oklahoma State University
Stillwater, Oklahoma 74078

365. *Unsegmented Continuous Flow Sample Processing and Electrochemical Detection and Determination of Gaseous Species*
H.A. Mottola **$65,000**
Department of Chemistry

This work involves a novel approach to sample processing in determining gaseous pollutants of oxidizing and reducing nature. A continuous-flow unsegmented all-gas carrier system and a segmented liquid-gas interface system will be constructed for sample introduction and transport to the detection/determination port. A regenerable electrode probe based on the redox characteristics of the iron(II) and iron(III) complexes with 1,10-phenanthroline and related ligands will be implemented as the detection device. Several electrodes of the chemically modified type will be constructed and tested. Amperometric and coulometric current measurements will be evaluated for acquisition of the analyte signal for quantitative purposes. Voltammetric studies will provide evaluation of the electrode surfaces generated as part of the work.

Purdue University
West Lafayette, Indiana 47907

366. *Reactions of Gaseous Metal Ions/Their Clusters in the Gas Phase Using Laser Ionization: Ion Cyclotron Resonance Spectroscopy*
B.S. Freiser **$115,000**
Department of Chemistry

Our recent developments (involving both software and hardware modifications of the Nicolet FTMS-1000 Fourier transform mass spectrometer) now enable us to conduct research in what can be properly termed a complete gas phase chemical laboratory. Selected ions of interest can be mixed with various reagents and their detailed chemistries monitored through a series of as many as eight reaction sequences. At any point in these sequences, ion structures can be elucidated and fundamental kinetic and thermodynamic parameters of the reactions can be determined. We are currently examining the gas phase chemistry and photochemistry of metal ions, metal clusters, and metal complexes, all of which have a bearing on the fundamentals of catalysis.

San Diego State University
San Diego, California 92182

367. *Development and Optimization of Methodologies for Analysis of Complex Hydrocarbon Mixtures*
R.J. Laub **$68,000**
Department of Chemistry

This project explores and further clarifies optimization methodologies for gas- and liquid-chromatographic separations of complex hydrocarbon mixtures. Emphasis is being placed at present on the kinetics of mass transfer, temperature effects, and mobile-phase composition in microbore-, conventional-bore, and rotating-disk thin-layer liquid-chromatographic techniques with silica, reversed-phase silica, and alumina adsorbents. Also being studied are metal-modified silica LC packings, including *in situ* generation, and alteration of the adsorbent surface. The utility of binary carriers in gas chromatography is being examined, where the second-interaction virial coefficients are predicted in advance. Solute retentions are then calculated, where the separations achieved are a function both of the carrier pressure and composition. Work on establishment of a standard set of stationary phases for gas chromatography is being continued, where emphasis is being placed on newly-synthesized mesomorphic polysiloxane solvents.

State University of New York/Stony Brook
Stony Brook, New York 11794

368. *Fundamental Studies in Isotope Chemistry*
J. Bigeleisen **$66,000**
Department of Chemistry

Experimental and theoretical investigations are made of isotope effects in chemical and physical processes. When appropriate, applications are made to isotope separation processes and nuclear fuel cycles. As part of a program to search for superheavy isotopes, detailed calculations have been made of the separation expected of superheavy isotopic forms of CO and NO by fractional distillation. Analysis of the ^{13}C and ^{17}O enrichment in a special run at the LANL ICONS facility to concentrate the X^- particle by distillation of CO shows excellent agreement with predictions. Experiments to determine the temperature coefficient of the liquid-vapor isotope fractionation factor in systems where the fractionation factor results primarily from a shift of the internal zero point energy on condensation have now been completed. The zero point energy difference between liquid and vapor is, to a first approximation, a linear function of the density difference between the phases. This result, combined with previous studies on the temperature dependence of the mean square force and mean square torque, leads to a scaling law for the logarithm of the liquid-vapor isotope fractionation factor. A complete theoretical system has been established for the systematization of the isotope chemistry of any element.

369. Stable Isotope Studies

T. Ishida **$91,000**
Department of Chemistry

This project involves basic studies of isotope effects (IE) and their applications to problems of stable isotope fractionation. We have successfully completed (1) the study of ^{15}N enrichment by isotope exchange between nitric oxide and dinitrogen trioxide and (2) the precision measurements of vapor pressure isotope effects (VPIE) in liquid methylene difluoride and in liquid and solid ammonia. Current areas of investigation include: (1) the anomalously large H/D-VPIE and small $^{12}C/^{13}C$ VPIE in liquid methylene fluoride correlated with weakly hydrogen-bonded structure of the liquid by means of *ab initio* molecular orbital calculations, (2) precision data on ammonia VPIE (H/D and $^{14}N/^{15}N$) analyzed in the light of extended cell model, (3) development of a self-contained chemicals recycle system to eliminate the need for external chemical feed and chemical waste disposal from ^{15}N fractionation processes, (4) development of a new type of heterogeneous catalyst for hydrogen isotope exchange reactions with the goal of application to heavy water production technology, and (5) the zero-point energy (ZPE) approximation method developed in previous years is applied to develop ZPE-additivity parameters for various homologs of organic molecules and to the transition state problems.

Syracuse University
Syracuse, New York 13210

370. Mechanisms of Gas Permeation Through Polymer Membranes

S.A. Stern **$80,753**
Department of Chemical Engineering and Material Sciences

The project objective is to investigate the mechanisms of gas permeation through rubbery and glassy polymer membranes. The significant changes that occur in these mechanisms at the glass transition temperature (T_g) of polymers are of particular interest. To investigate the character of these changes, permeability, diffusion, and solubility coefficients for CH_4, C_2H_6, and η-C_4H_{10} in poly(eta-butylmethacrylate) are being determined over a wide range of pressures and a range of temperatures encompassing the T_g of this polymer ($T_g \simeq 27°C$). Four different types of measurements are being made for this purpose, using the time-lag and electromicrobalance techniques at low pressures and the steady-state permeation and isobaric gas absorption techniques at high pressures. A transition in permeation mechanism from a free-volume behavior to a dual-mode sorption behavior was observed as the temperature was lowered through T_g. The measurements below T_g were history-dependent, probably due to slow relaxation phenomena in the polymer. These effects were particularly marked in the case of C_3H_8, which exhibits the highest solubility in the polymer as compared to the other penetrant gases investigated. A generalized permeation model applicable to temperatures both above and below T_g has been developed, and its validity will be tested experimentally.

371. Reactor Analysis for Selective Metal Ion Extraction in Liquid Dispersions

L.L. Tavlarides **$120,000**
Department of Chemical Engineering and Material Sciences **(18 mo.)**

The goal of this project is to provide fundamental models for the rational design of liquid extraction processes to predict conversion and selectivity in the hydrometallurgical extraction of metals. The dispersed phase model we developed incorporates the details of the thermodynamic chemical equilibria, chemical kinetics, mass transfer processes, and the effects of droplet mixing. The project has a two-fold objective. First, the effects of droplet mixing on conversion and selectivity will be quantified. Bivariate drop size concentration data for the Co^{+2}-NO_3^--di(2-ethylhexyl)phosphoric acid system will be obtained in a continuous flow stirred tank extractor. A specially designed capillary laser spectrophotometer is under construction for this purpose, and thermodynamic equilibrium and kinetic data are being generated. A Lewis cell contactor was constructed for kinetic data acquisition. Comparison of experimental results with simulation analysis will confirm the validity of the models and suggest improvements. The second objective is to extend the models to analyze multistage extractor performance for various configurations. Although the analysis will be made for the Co^{+2}-Ni^{+2} multiple metal system, model applicability to other complex hydrometallurgical systems is straightforward.

372. Particle Deposition in Granular Media

C. Tien **$95,000**
Department of Chemical Engineering and Material Sciences

The principal objective of this study is to elucidate the various phenomena arising from the flow of aerosol suspensions through and the deposition of aerosols in granular media. The project focuses on (1) experimental investigation of the transient behavior of aerosol filtration in granular filters, (2) development of algorithms for predicting aerosol filtration in fluidized beds, (3) aerosol collection in magnetically stabilized fluidized filters, (4) *in situ* observation of aerosol deposition in two-dimensional model filters, and (5) experimental study of cross-flow moving-bed granular filtration.

University of Tennessee
Knoxville, Tennessee 37996-1600

373. *Systematic and Structural Studies of Polymeric Extractants for the Separation and Recovery of Metal Ions*

S.D. Alexandratos **$84,112**
Department of Chemistry

A new class of resins, which we have termed dual mechanism bifunctional polymers, has been synthesized. The primary application for these resins is the recovery of metal ions from aqueous streams using solid-liquid extraction schemes. They can be effectively utilized in hydrometallurgical processes and are especially important for strategic metal recovery. These resins consist of a polystyrene support network on which are bonded two different phosphorus groups. When brought in contact with a metal-containing aqueous stream, they ion-exchange with the metal cation and then reduce it, allowing the isolation of zerovalent metal. These high capacity, stable resins may be produced in two steps from polystyrene beads and show a great affinity for transition metal ions; they will absorb 70% of the mercuric ions in solution under conditions where commercial sulfonic acid resins absorb 25% and carboxylic acid resins absorb 15%. Additionally, these resins release the mercury after the reduction reaction, allowing it to collect in a reservoir apart from the resin itself. The selective recovery of metallic silver and gold from aqueous solutions has also been accomplished.

374. *Capillary Separations with Calorimetric Absorbance Detection*

M.J. Sepaniak **$57,700**
Department of Chemistry

The project objective is the development and use of laser-based detection techniques in microscale liquid chromatography. Fluoroescence detection has been used extensively to evaluate chromatographic columns prepared in our laboratory. Thermal lens detectors employing single beam and pulsed double beam optical configurations have also been developed. The single beam configuration was used to sensitively detect nitroaniline compounds, which were separated using bonded-phase open tubular columns. We are using a pulsed heating laser beam and a perpendicularly oriented cw probe laser beam to detect nitropyrene isomers, which we separate using packed fused silica columns. Detection limits for 1-nitropyrene are in the low pg injected range, with baseline noise levels less than 10^{-6} absorbance units. Most recently we have constructed a small volume photoconductivity flow cell, compatible with many of our microscale chromatography columns. We also have demonstrated the utility of dynamically modified open tubular columns for bio-separations. Dynamic modification is accomplished by incorporating a surfactant in the mobile phase, which interacts with silanol groups on the inside surfaces of our columns to form a stationary phase. We have also begun to explore the use of micellar electrokinetic chromatography. Using 0.75 m open tubular columns with liquid phases containing SDS micelles, we have generated efficiencies in excess of 60,000 theoretical plates.

Texas A and M University
College Station, Texas 77843-3255

375. *Investigations on Multiphoton Ionization and Fast-Beam Photodissociation Spectroscopy*

D.H. Russell **$97,500**
Department of Chemistry **(15 mo.)**

This project emphasizes laser-ion beam photodissociation methods for probing the dynamics of dissociation reactions of highly activated ionic systems. The experimental hardware and methods are being developed by using model chemical systems such as $C_6H_6{}^+$ and $C_4H_4{}^+$, which are relatively well characterized, and new systems such as $Fe_x(CO)_y{}^+$ and similar ionic cluster fragments. In addition, the potential analytical utility of laser-ion beam photodissociation for the structural characterization of large biomolecules is being evaluated. These latter studies are being performed on ions formed by fast-atom bombardment (FAB) ionization and include molecules such as chlorophyll a, vitamin B_{12}, small peptides, and glycopeptides (1500 to 4000). These studies are performed on modified analytical instruments (e.g., Kratos MS-50TA and MS-902) as well as a Fourier transform mass spectrometer (Nicolet FTMS-1000).

University of Texas at El Paso
El Paso, Texas 79968-0513

376. *Macrocyclic Lanthanide Ion Selective Reagents*

C.A. Chang **$52,000**
Department of Chemistry

Previously, we have shown that the ligand, 1,10- diaza- 4,7, 13,16- tetraoxacyclooctadecane- N,N′- diacetic acid (1), is selective toward the lighter lanthanide ions as a group (i.e., La^{+3}, Ce^{+3}, Pr^{+3}, Nd^{+3} ions). Similarly, we have determined the formation constants of Ln- complexes of the macrocyclic ligand, 1,7- diaza- 4,10, 13- trioxacyclopentadecane- N,N′- dia cetic acid (2), which has a smaller cavity size as compared to (1), and the europium(III) complex has been found to be the most stable of all the lanthanides. The stopped-flow kinetic studies of complexes of (2) in buffered aqueous solutions, indicate that their dissociation proceeds by two detectable pathways (the direct dissociation and the acid catalyzed dissociation). For complexes of the lighter lanthanides, the observed rate constants are related to the acid concentration by the expression, $k_{obs} = + k_d + k_H [H^+]$, whereas the kinetics for heavier lanthanide complexes is more complex, attaining a limiting rate at high $[H^+]$. Current emphasis is on elucidation of complex structures in solution and as solids using a laser fluorescence technique. Study of synergistic extractions of complexes of (1) and (2) into organic solvents is also in progress.

Texas Tech University
Lubbock, Texas 79409

377. *Use of Functionalized Surfactants in Flame Atomic and Luminescence Analysis*

D.W. Armstrong **$65,000**
Department of Chemistry

Nine functionalized surfactants have been used in this project to enhance the sensitivity and selectivity of a variety of techniques including chromatography, luminescence, Raman, atomic absorption, and emission analysis. Conventional surfactants such as sodium dodecyl sulfate and cetyltrimethylammonium bromide have shown some success in improving these methods. The mechanism by which these surfactants produce their effects has been the subject of controversy. Using specially designed surfactants, we have been able to improve the sensitivity and applicability of some techniques. The functionalized surfactants are useful in luminescence and ion chromatography. Perhaps the most exciting discovery involves the use of these surfactants in micellar enhanced resonance Raman spectroscopy. Resonance Raman currently is beset with problems (e.g., high background, interferences, and so forth). As a result of this new development, resonance Raman analysis may evolve into a sensitive, widely applicable analytical technique.

378. *Metal Ion Complexation by Ionic Crown Ethers*
R.A. Bartsch **$82,000**
Department of Chemistry

The goals of this research are the synthesis of lipophilic crown ethers with pendant ionizable groups and the application of these compounds for selective metal ion complexation. A variety of lipophilic ionizable crown ethers are being prepared in which the following structural features are systematically varied: (1) the size of the polyether cavity; (2) the number and types of ethereal oxygens in the crown ether ring; (3) the attachment site(s) for lipophilic groups; (4) the presence or absence of aromatic groups as polyether ring substituents; and (5) the type of ionizable group. The ionizable functions include carboxylic, phosphonic, and sulfonic acid groups. The efficiencies and selectivites of these lipophilic ionizable crown ethers in competitive solvent extraction, liquid surfactant (emulsion) extraction, and bulk liquid membrane transport of alkali metal, alkaline earth, and transition metal cations are being assessed.

379. *Novel Approaches to Ionic Chromatography*
P.K. Dasgupta **$87,500**
Department of Chemistry **(15 mo.)**

The project objective is to develop analytical methodology for high resolution, high sensitivity chromatographic analysis of ions. In pursuing membrane suppressor based ion chromatography, very low dead volume and low dispersion dual membrane devices have been successfully fabricated which can ion exchange high input fluxes quantitatively. In one design, a filament filled membrane tube is inserted inside another membrane tube and the whole coiled into a small diameter helix. Regenerant flows through the inner membrane and outside the outer membranes. In another design, the inner membrane tube is filled with inert or ion exchange beads to form a single bead string reactor inserted inside another membrane tube, and the whole assembly is put inside a concentric rigid shell. The void space in the shell is also filled with beads. This dual annular geometry exhibits superior fluid phase mass transfer rates compared to other available designs for membrane based separation processes and, as such, is likely to have applications other than chromatography. Similar membrane based devices are being tested for the removal of CO_2 from ion exchanged eluents. Other areas being studied include the utility of fluorogenic ligands in cation chromatography and the use of diode array detectors combined with flow injection analysis to rapidly yield quantitative information about metal-ligand equilibria.

University of Utah
Salt Lake City, Utah 84112-1183

380. *Fourier Transform Photoacoustic Spectroscopy*
E.M. Eyring **$78,000**
Department of Chemistry

Microphonic photoacoustic spectroscopy (PAS) has proven to be a useful analytical tool for qualitative identification, and in favorable situations, quantification of chemical species adsorbed at a gas-solid interface or at shallow depths (< 1 mm) in the bulk solid. Among the disadvantages of the technique are its unsuitability for detection of fast transient chemical species or work at high gas pressures and under vacuum and the difficulty of microphonic measurements at elevated temperatures. Two other photothermal spectroscopies, photothermal beam deflection (PBD) and photothermal radiometry (PTR), have lately emerged that appear capable of circumventing these limitations. FT-IR/PBD spectral studies of organic polymers selected for their opacity and comparative chemical simplicity are being carried out over an extended range of temperatures and pressures. The objective is the determination of the basic chemistry required for FT-IR/PBD spectroscopy to surpass FT-IR/PAS in usefulness. A by-product of the resulting infrared spectral information will be an improved understanding of doping of semiconducting organic polymers. Some of the same polymer samples are being reexamined by PTR using pulses of visible radiation from flash lamp pumped wavelength tunable dye laser to excite the sample and HgCdTe detectors to measure emitted radiation.

381. *Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species*
J.D. Miller **$65,000**
Department of Metallurgy and Metallurgical Engineering

The separation of nonsulfide minerals from ore is frequently accomplished by froth flotation using unsaturated fatty acids as collector. Variables such as temperature, oxygen partial pressure, and solution chemistry may have a significant effect on flotation rate and the hydrophobic character of certain nonsulfide minerals. Bubble attachment measurements at a fluorite (CaF_2) surface have shown that attachment times decrease by an order of magnitude at higher temperature and higher oxygen partial pressure when compared to ambient conditions. Adsorption density measurements indicate that chemisorption reactions occur between oleate and the fluorite surface. At higher temperature and oxygen potential the adsorption density increases slightly. More important, however, is the finding from infrared spectroscopy that the carbon–carbon double bond is reduced in intensity under these conditions, indicating a specific interaction of the adsorbed unsaturated collector species. Study of the nature of this interaction is in progress; it has been established that the oleate interaction at the fluorite surface consumes oxygen. It is thought that the interaction may involve surface polymerization; if such a reaction is operative, the implications are far-reaching. Catalysts or new collectors can be developed to improve the performance, selectivity, and energy-economy in nonsulfide mineral flotation systems.

University of Virginia
Charlottesville, Virginia 22901

382. *Glow Discharge as an Atomization and Ionization Source*
W.W. Harrison **$80,000**
Department of Chemistry

This project studies the glow discharge as an atomization and ionization source. Of interest is the development of the discharge as a source for the trace element analysis of solids by mass spectrometry and atomic emission. A tunable pulsed laser will serve as a sensitive, selective ionization device for atoms sputtered from a cathode sample. A pulsed glow discharge synchronized with the pulsed laser will be studied as an enhanced atomization source. The pulsed discharge will also be studied as a direct elemental analysis source by glow discharge mass spectrometry. We will also develop the hollow cathode plume as a new source for atomic emission and mass spectrometry, including pulsed operation. These studies have many complementary aspects in terms of elucidating the fundamental properties of the glow discharge and applying this device to trace element analysis.

Washington State University
Pullman, Washington 99164-4630

383. *Studies of the Analyte-Carrier Interface in Multicomponent Flow Injection Analysis*
S.D. Brown **$60,000**
Department of Chemistry

The use of flowing streams to transport injected analytes has received considerable attention lately. Situations where the injected analyte reacts with reagents present in the carrier stream have received almost no study. This project involves the study of product distributions with an injected bolus. Initial studies have focused on the characterization of the flow reactor and on the development of software for the analysis of mixtures and for the study of reaction kinetics. These studies will be useful in analyses of the distribution of reaction products across the interface of the injected bolus and the carrier stream in flow injection analyses.

University of Wyoming
Laramie, Wyoming 82071

384. *Solid Surface Luminescence Analysis*
R.J. Hurtubise **$115,000**
Department of Chemistry

The goal of this project is to develop a fundamental understanding of the physical and chemical interactions that induce strong room-temperature fluorescence and phosphorescence from organic compounds adsorbed on solid surfaces. Reflectance, infrared, and luminescence spectroscopy are being used to clarify the interactions. The effects of moisture, several gases, and temperature on the luminescence intensities and the phosphorescent lifetimes of adsorbed compounds are being investigated. In addition, a method is being developed for the determination of the fluorescence and phosphorescence quantum efficiencies of organic compounds adsorbed on solid surfaces. The results from the various experiments will help to determine whether the luminescent molecules are held rigidly or if the solid matrix prevents collisions with oxygen and water molecules. Other work involves use of cyclodextrins to induce room-temperature luminescence from adsorbed compounds and use of solid-surface luminescence to study interactions in adsorption chromatography.

Chemical Engineering Sciences

Brigham Young University
Provo, Utah 84602

385. *Thermodynamic Study of CO_2-Organic Compound Interaction at High Pressures and Temperatures*
J.J. Christensen, R.M. Izatt **$100,000**
Department of Chemical Engineering **(15 mo.)**

The primary objective of this project is to elucidate the energetics associated with the interaction of CO_2 and freons with selected organic compounds under temperature-pressure conditions where either one or more of the components is in its supercritical region. The quantities measured are heats of mixing (H^E) of binary mixtures using flow calorimeters. The temperature and pressure ranges covered are 285 to 673 K and 8 to 12.5 MPa, respectively. The data allow evaluation to be made of the effect of temperature and pressure on the magnitude of H^E and on phase splitting. The occurrence of phase splitting is detected by discontinuities in the H^E curves, and the phase compositions are calculated from the mole fraction values at the points of discontinuity. In the critical region, large variations in H^E are found with temperature, pressure, and component mole fraction. Moreover, the H^E values show large positive or negative values as the critical region is spanned. The large changes in H^E have been modeled successfully using the Andrews-Soave and other equations of state. The eventual goal is to elucidate the chemistry occurring in super-critical fluid processes.

University of California
Davis, California 95616

386. *Statistical Modeling and Analysis of Chemically Reacting Turbulent Flows*
H.A. Dwyer, W. Kollmann **$89,900**
Department of Mechanical Engineering

This project seeks to develop new turbulent closure models for variable density turbulent flow and turbulent diffusion flames. The methods used to accomplish these goals are (1) physical and mathematical modeling and (2) sensitivity analysis. The modeling techniques cover the closure of density-velocity statistical correlations and the use of Monte Carlo simulations for scalar transport. The research has centered on turbulent jets, but a new effort on boundary layer flows has been initiated. Sensitivity analysis studies have been extended to variable density and combustion flows; the results provide insight into the complex interaction between combustion and turbulent flow.

University of California
Santa Barbara, California 93106

387. Reaction Enhancement of Heterogeneously Catalyzed Reactions by Concentration Forcing
R.G. Rinker **$64,000**
Department of Chemical and Nuclear Engineering

An investigation is underway to examine experimentally the underlying phenomena leading to enhancement of heterogeneously catalyzed reaction systems by periodic concentration cycling of reactants (concentration forcing). Several consequences of periodic cycling, compared to conventional steady-state operation for reactions with nonlinear pathways, include (1) higher time-averaged product yields, (2) longer catalyst life, (3) improved catalytic selectivity, and (4) lower energy costs. The results of this study, which is focusing on the synthesis reactions of ammonia and menthanol, are expected to provide new insight into how surface concentrations of reactants on catalysts can be manipulated under conditions of practical interest to kinetically accelerate the rate-limiting step(s) in the overall conversion. The results are also expected to provide new directions for catalyst design. Kinetic and thermodynamic parameters of the selected reactions, for use in modeling unsteady-state operation, are obtained in a differentially-operated fixed-bed reactor by transient experiments capable of distinguishing among individual phenomenological steps. Mathematical simulations of integral fixed-bed reactors having plug flow or perfect mixing in the fluid phase and operated under periodic cycling conditions (either isothermally or adiabatically) are being used to compare alternate inlet conditions including pulse widths, frequencies, and compositions. Results of the simulations are being compared to the experiment.

California Institute of Technology
Pasadena, California 91125

388. Dynamics of Vapor Explosions
B. Sturtevant **$51,500**
Graduate Aeronautical Laboratories

The effect of ambient pressure on the dynamical behavior of a single droplet (1 to 2 mm diameter) of volatile liquid boiling explosively at the limit of superheat is studied both experimentally and theoretically. In a series of experiments with pentane, isopentane, ethyl ether, and butane it was shown that the evaporative instability is suppressed at high pressure. At intermediate pressures bubble growth occurs in two stages; first stable, then unstable. Pressure measurements show that the radiated pressure field is two orders of magnitude larger from unstable bubbles than stable. Direct evidence is obtained showing that during violently unstable boiling small liquid particles are torn from the liquid-vapor interface. This ejection of fine droplets from the evaporating surface produces a mass flux orders of magnitude greater than that characteristic of ordinary boiling. The Landau mechanism for the instability of laminar flames is adapted to the case of evaporation to investigate the effects of variable ambient pressure in both planar and spherical geometry. Planar theory yields results in general agreement with observation. The sensitivity of the instability to temperature suggests that small temperature nonuniformities may be responsible for quantitative departures of the behavior from predictions.

City College of New York
New York, New York 10031

389. Turbulence and the Distortion of Reactions
J.A. Johnson **$80,000**
Department of Physics

Contact surfaces in a pressure-driven shock tube are used as a way of investigating the possibility of the manipulation of molecular recombinations. Turbulent bursts are produced. The reaction $2NO_2+X \rightarrow N_2O_4 + X$ ($X = N_2$ or Ar) is unstable under some circumstances; fluctuations with amplitude incoherence and phase coherence are developed. Here, the use of standard reaction rate data proves to be inadequate. The point-resolved histories of density, velocity, and other flow and mixture properties are determined, using cross-beam correlations and fluorescence of NO_2 probed by the 4.88 nm line from an Ar^+ ion laser. The importance of the dynamical parameters of turbulence is being measured; specifically, the impact of changing local viscosity, characteristic turbulence scale, and turbulence intensity. In addition, there is some evidence that a reduced molecular chaos may be relevant to this kind of process. This possibility is given a quantitative formulation and tested in our data.

Columbia University
New York, New York 10027

390. Interaction of Turbulence and Chemical Reactions
R. Chevray **$92,600**
Department of Mechanical Engineering

Flow in a two-dimensional mixing layer is utilized to study a well-known reaction with simple kinetic scheme. The flow represents a well-defined turbulent situation, and additional complexities of finite heat release are avoided by use of small concentrations for the reaction chosen ($NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu + O_2$). Large Reynolds numbers, small dilution numbers, large reaction speed numbers, and several concentration ratios are investigated. Conditional and conventional measurements are made of mean and fluctuating quantities for both the velocity and concentration fields by laser Doppler anemometry and fiber optics absorption spectroscopy, respectively. Simultaneous cinefilm recording is conducted to determine the convection velocity of the interface and hence the entrainment. Numerical simulation is set up to model directly the equations describing the evolution of the species concentration in the shear layer.

Cornell University
Ithaca, New York 14853-0294

391. Experimental and Theoretical Studies of Dense Fluid Mixtures
W.B. Streett, K.E. Gubbins **$218,000**
School of Chemical Engineering **(24 mo.)**

The primary goals of this research are: (1) to carry out wide-ranging thermophysical property measurements for pure fluids and mixtures and (2) to develop improved methods for correlating, extrapolating, and predicting dense fluid properties using statistical mechanics and intermolecular potential theory. Recently completed experimental research includes measurements of the PVT properties of CF_4 and CHF_3 at pressures to 1000 bars. The direct-weighing PVT apparatus, designed and built under this project, has been completely redesigned and reconstructed to extend the temperature and pressure ranges to 0 to 600°C and 0 to 2000 bars, respectively, and is being used to study CCl_4. Measurements of the velocity of sound in fluids over wide ranges of pressure and temperature have been initiated in 1984-1985, with measurements on CCl_4. Theoretical work has included development of statistical mechanical methods for calculating the effects of molecular polarizability, including complicated multibody induction effects. These effects have been found to be almost an order of magnitude larger than anticipated on the basis of dilute gas calculations.

University of Delaware
Newark, Delaware 19716

392. *The Generalized van der Waals Theory of Pure Fluids and Mixtures*

S.I. Sandler **$65,000**
Department of Chemical Engineering **(15 mo.)**

The generalized van der Waals theory provides an excellent framework for understanding the basis for applied thermodynamic models currently in use and deriving new, improved models with potential application to heavy oils, coal liquids, and other synthetic fuels. Using a form of the generalized van der Waals partition function that we developed, we now understand the molecular-level assumptions explicit or implied in current thermodynamic models. Further, using computer simulation and integral equation theory, we can test these assumptions, establishing the theoretical validity of some and errors in others, especially some of the recently proposed local composition models. We can also make significant improvements in several models using the combination of the generalized van der Waals theory, integral equation theory, and computer simulation. Work focuses on developing new equations of state, mixing rules, and activity coefficient models for mixtures of molecules of widely differing size and functionality. An important feature of these models will be their firm theoretical basis and broad range of validity.

University of Florida
Gainesville, Florida 32611

393. *Theoretical and Experimental Investigations of Fluctuation Thermodynamic Properties of Liquid Solutions*

J.P. O'Connell **$85,000**
Department of Chemical Engineering

Fluctuation solution theory will be developed for analysis and application to strongly nonideal liquid mixtures, including electrolytes. The work includes both theoretical analysis, and correlation and experimental measurement using ultracentrifuge equilibrium distribution, concentration fluctuations from light scattering, and liquid volumes. The results will provide benchmarks for both complete equations of state and statistical mechanical and computer simulation treatments of such systems. In addition, useful correlations will be completed for process design in important energy-related processes such as fossil fuel recovery, high pressure reaction and separation systems (including coal conversion and petrochemical hydrogenation), energy storage devices, extraction and crystallization devices (as in hydrometallurgy), and geologic systems for geothermal power production and mining. The method will also be of use in environmental problems such as industrial waste processing and metallurgical recovery. The project objectives are (1) to complete a theoretical basis for properties of liquids that is rigorous while leading to useful correlations and (2) to establish both a formulation and a data base that others can use for sensitive comparisons with their methods for strongly nonideal liquids.

Hokenson Company
Los Angeles, California 90005

394. *Coherent Structure: Reflective Turbulence Modeling of Complex Shear Flows*

G.J. Hokenson **$19,700**
Fluid Mechanics and Heat/Mass Transfer Division

The limitations of turbulence modeling with respect to the accurate prediction of complex shear flows will be analyzed. The flowfield effects of interest are associated with combustor flows and include strong pressure gradients, streamline curvatures, and density gradients. Each effect will be considered alone and in combination with others to isolate the modeling implications regarding: (1) basic turbulent structures, (2) gradient transport, and (3) isotropy. Of particular interest is the strong turbulence suppression or enhancement that each effect may induce, involving the possible generation of wave-like features with a corresponding non-diffusive and highly anisotropic nature. The project objective is to provide a framework for future research in which successful turbulence modeling prescriptions may be carried over to a multiple-element representation of the flow. In such a formulation, the physics of processes occurring at various scales and coherences may be differentiated from each other and depicted in a manner faithful to the experimental data. The practical utility of such an approach in providing accurate predictions of untested flows would then be tested.

University of Illinois
Chicago, Illinois 60680

395. *Development of the Analytic Variational Inequality Minimization (VIM) Equation of State*

G.A. Mansoori **$64,200**
Department of Chemical Engineering

This research concerns the development of an analytic equation of state for polar, quantum and associated fluids and fluid mixtures of practical interest. The approach is based on the variational inequality minimization (VIM) theory of statistical mechanics. The objectives of this research include the following: (1) extension of the VIM equation of state to pure fluids of polar and associated molecules due to hydrogen bonding; (2) extension of the applicability of the VIM equation of state to quantum fluids; (3) calculation of a set of intermolecular potential energy parameters based on the VIM theory for use in the VIM equation of state; and (4) extension of the VIM equation of state to mixtures.

Johns Hopkins University
Baltimore, Maryland 21218

396. *Prediction of Thermodynamic Properties of Coal Derivatives*

M.D. Donohue **$83,000**
Department of Chemical Engineering

The purpose of this project is to develop an equation of state to predict the thermodynamic properties of coal derivatives. The equation is based on perturbed hard-chain theory, but includes additional terms for multi-pole interactions. The equation allows prediction of vapor pressures, densities, and solubilities for a wide range of organic molecules including multiringed aromatics. Pure component and mixture parameters are determined from experimental data when available; a group-contribution correlation is being developed to allow prediction of parameters for systems where no experimental data are available. The applicability of the new equation to supercritical fluid extraction is being studied. Hydrogen bonding effects are being taken into account to predict properties of systems containing H_2O, alcohol, and so forth. High pressure vapor-liquid equilibrium measurements for CO_2- aromatic binary mixtures are being made.

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

397. *Thermodynamics and Rate of Methanol Conversion to Hydrocarbon on Zeolites*

R.A. Alberty **$168,400**
Department of Chemistry **(24 mo.)**

The objective of this project is to determine the extent to which thermodynamics can account for the distribution of products in the gasoline produced from methanol using zeolite catalysts, and the way in which deviations from equilibrium can be accounted for in terms of rate constants. These calculations are made using isomer groups and linear restrictions in a general equilibrium program. Calculations are made for various temperatures, pressures, catalyst selectivity, and extent of reaction. In order to make these calculations, tables of isomer group thermodynamic properties are produced, and the Benson method is used to augment literature data. Thermodynamic data on higher isomer groups are obtained by linear extrapolation. Chemical equilibrium calculations have been made separately on two homologous series in the gasoline produced from methanol: the alkylbenzenes and alkenes. In order to account for the experimental data in both cases, certain bulky species must be omitted from the calculation because of the selectivity of the zeolite catalyst. New methods for making chemical equilibrium calculations using homologous series groups and continuous thermodynamics are being developed.

National Bureau of Standards
Boulder, Colorado 80303

398. *Experimental and Theoretical Study of the Thermophysical Properties of Fluid Mixtures*

H.J.M. Hanley **$225,000**
Chemical Engineering Science Division

The project combines experiment, theory, and correlation to study the properties and behavior of fluids. Specific objectives are to produce PVT and thermodynamic data on hydrocarbon fluids and their mixtures at high temperatures (to 900 K) and pressures (to 35 MPa, possibly to 100 MPa) so as to (1) develop the theory of liquids and (2) develop models to predict the properties based on the theory and optimized by the data. PVT properties of H_2S and propane have been published; properties of methanol have been measured. Phase equilibria VLE measurements of the system CO_2-i-butane also have been published. Theoretical studies include computer simulation of fluids under shear for which several results have been published. A thermodynamics for a shearing system has been proposed. Predictions of shear induced phase transitions in liquid-gas and liquid-liquid mixtures have been discussed. Plans include PVT studies of benzene and further computer simulation studies of mixtures.

National Bureau of Standards
Gaithersburg, Maryland 20899

399. *Transport and Phase Equilibria in Multicomponent Fluids*

J.M. Kincaid **$89,000**
Division of Thermophysics

The purpose of this project is to develop and implement simple, accurate techniques to treat the transport and phase transition properties of multicomponent systems. The main focus has been: (1) to develop a thorough characterization of the Enskog theory of hard-sphere mixtures and to determine how the hard-sphere theory can be used to predict the transport coefficients of real fluids and (2) to develop new methods for solving the phase equilibrium conditions of multicomponent systems based on the so-called polydisperse (continuous) fluid formalism. Recent progress includes: (1) a complete analytical exposition of the Enskog theory for mixtures; (2) a thorough study of the mutual diffusion coefficients of binary and ternary mixtures; (3) a mathematical study of polydisperse fluids demonstrating the ways in which the polydisperse formalism is equivalent to the usual multicomponent fluid approach; (4) the solution of two common phase equilibrium problems: solvent + polydisperse impurity and the nearly monodisperse fluid; and (5) a derivation of the critical-point conditions for a polydisperse fluid.

University of Pennsylvania
Philadelphia, Pennsylvania 19104

400. *Thermodynamics of Systems of Very Many Components*

E.D. Glandt **$84,500**
Department of Chemical Engineering

This theoretical research concerns the thermodynamic and structural behavior of polydisperse fluid mixtures such as liquid fuels and polymer solutions and melts. The continuous Lennard-Jones model substance is an appropriate representation of the former, and is being investigated through a perturbation theory for narrow cuts and through Monte Carlo computer simulations. Both types of studies have been carried out for successively wider distribution functions. These continuous mixtures were found to be increasingly non-ideal and their properties (equation of state, internal energy, and so forth) to be increasingly different from those of the reference substance(the pure, most abundant component at the same density and temperature). Two different polydispersity regimes were identified. For very narrow cuts, all properties were found to be extremely sensitive to the width (the second moment) of the distribution. As the distribution becomes wider, a saturation phenomenon occurs and the thermodynamic properties become totally insensitive to the details of the composition distribution function. These two contrasting types of behavior are now being modeled and studied separately.

Purdue University Research Foundation
West Lafayette, Indiana 47907

401. *Gas-Liquid-Liquid Equilibria in Mixtures of Water, Light Gases, and Hydrocarbons*

K.C. Chao, H.M. Lin **$70,000**
School of Chemical Engineering

Phase equilibrium in mixtures of water + light gases and water + heavy hydrocarbons will be investigated in light of recent advances of group contribution, equation of state, and local composition. In order to develop quantitative models of water solutions, an experimental study will be made of gas-liquid equilibrium at temperatures up to 430°C and pressures to 300 atm and of liquid-liquid equilibrium at temperatures up to 250°C. Construction of a new vapor-liquid equilibrium cell has been completed and tested to 5000 psia. The cell is equipped with sapphire windows for investigation of mixtures of water at high temperatures and pressures. A literature survey for experimental data of vapor-liquid and liquid-liquid equilibria on mixtures containing water has been completed. Measurements of liquid-liquid equilibria have been completed for water + thianaphthene and water + 9, 10-dihydrophenanthrene over the temperature range of 60 to 220°C at 20° intervals.

Stanford University
Stanford, California 94305

402. *Fundamental Studies of Heat Transport, Fluid Mechanics, and Stability in Porous Media*

G.M. Homsy **$191,200**
Department of Chemical Engineering **(24 mo.)**

This project treats problems in flow and transport phenomena in porous media whose solutions are of interest in energy recovery processes. Both macroscopic and microscopic problems are being addressed. Most of our macroscopic work has focused on viscously driven instabilities, so-called fingering, which occur in displacement processes. Experiments in Hele-Shaw cells have shown good agreement with theoretical predictions of the initial development of fingers. We have discovered an intriguing tip-splitting instability of large-scale fingers. We are currently working on a theory of fingering in miscible displacements. Microscopic modeling of non-Newtonian flow in porous media has been studied, indicating that constitutive equations of the Oldroyd type are incapable of capturing the salient experimental features of these flows. New studies of blob dynamics in constricted-tube models of porous media have begun.

State University of New York/Stony Brook
Stony Brook, New York 11794

403. *Thermophysical Properties of Multiphase Systems*

G.R. Stell **$180,000**
Department of Mechanical Engineering **(24 mo.)**

Ongoing research to obtain the transport properties of fluids and fluid mixtures in analytically tractable form has continued. Two general approaches have been used. The first is a conditional-probability approach that yields a description of solvent-solute collision involving reduced mass and collision diameter renormalized by the presence of the solvent background. In the limit of identical solute and solvent particles, this has resulted in a new pure-fluid theory as well. A second general approach is information theoretic, based upon the maximization of entropy subject to increasingly refined constraints. This yields a sequence of successively more refined versions of a kinetic variational theory. When the pair potential includes a hard-sphere reference-potential term, the theory can be further improved by insertion of an improved treatment of the correlation induced by core-core collisions, yielding a sequence of kinetic reference theories. General expressions for transport coefficients from the variational and reference theories have been obtained and are being quantitatively evaluated.

University of Washington
Seattle, Washington 98195

404. *Experimental Determination of the Mixing Frequency Parameter for Coalescence/Dispersion Modeling of Turbulent Combustion*

G.W. Butler **$75,000**
Department of Mechanical Engineering

The project objective is to develop a fluid mixing rate model that incorporates the strong coupling between fluid and chemical dynamics typical of high intensity combustion processes. The physics of the mixing process will be investigated using stimulus-response techniques developed in nonreacting flows and applied to a carefully controlled combustion process. Rayleigh scattering optical techniques will be used to simultaneously measure the input and output concentration history of an inert gas injected into the reactant stream of a high-intensity jet-stirred reactor. The fluid time scales associated with the reactor will be varied using combinations of similar reactor geometries and flow rates, while the chemical time scales will be regulated using carbon monoxide, oxygen, and small amounts of hydrogen as a chemical throttle. A Fourier transform of the nonsteady injectant input and exhaust profiles will yield the reactor transfer function (in the frequency domain), which contains information related to the fluid mixing time scales. Correlations among the dominant frequencies of the transfer function, fluid time scales (viscous and inviscid), and the system chemical time scales then will be investigated. Stimulus-response experiments have been carried out in cold flow (no reaction) through a jet-stirred reactor and have demonstrated the viability of this experimental approach. With cold flow data as a basis for comparison, initial combustion experiments are proceeding.

University of Wisconsin
Madison, Wisconsin 53706

405. Interphase Transport and Multi-Stage Separations
W.E. Stewart **$78,000**
Department of Chemical Engineering

The project goal is to provide new physical understanding of stagewise separation processes and efficient algorithms for use in computer-aided design and operation of these processes. The physical studies include boundary-layer scaling analysis and multicomponent transport theory; the algorithmic studies include new collocation and continuation methods. Results from the first year of research will include: (1) asymptotic expansions for heat and mass transfer rates in laminar and turbulent flows, derived without recourse to eddy diffusivities or other closure approximations; (2) a new construction of practical linear laws for constrained multicomponent heat and mass transport (diagonability and uniqueness are secured without the usual assumption of stability with respect to diffusion); and (3) a new method for optimal design of distillation columns, using a fast low-order collocation scheme.

Heavy Element Chemistry

Florida State University
Tallahassee, Florida 32306

406. Research in Actinide Chemistry
G.R. Choppin **$15,000**
Department of Chemistry

This research is concerned primarily with complexes of actinide elements in aqueous solution. To supplement data on trivalent actinides, similar systems are investigated for trivalent lanthanides using the wider variety of techniques available with the latter elements. Our studies include measurements of the thermodynamic parameters of complexation of both inorganic and organic ligands, the kinetics of complexation, the spectroscopic properties of complexed species using electronic (f-f) transitions and nuclear magnetic resonance, and the redox properties of the actinides. The effect of decreased stability with increasing chelate ring size for alkyl dicarboxylate complexes has been shown to be an entropy effect. Polarization of negative charge to carboxylate binding sites was demonstrated to involve both resonance and inductive effects in the ligands. Reduction of neptunium(VI) occurs via the phenolic group of aromatic organic ligands, but not the carboxylate. However, reduction by dicarboxylate ligand occurred for the 1:1 metal-to-ligand complex, but not 1:2 and above. Direct calorimetry with ^{248}Cm has provided better values for the ΔH and ΔS of complexation with acetate and EDTA. Kinetic studies of dissociation of the thorium-humate indicate several different binding sites.

University of New Mexico
Albuquerque, New Mexico 87131

407. Development of Surface Immobilized Ligands for Actinide Separations
R.T. Paine **$73,000**
Department of Chemistry

The project objectives have been to develop systematic synthetic methods for the formation of new classes of soluble extractants and for the production of solid immobilized extractants, as well as to derive new materials for selective ion chromatographic separations of metal ions present in nuclear fuel reprocessing and industrial waste solutions. Fundamental investigations of steric and electronic effects that influence and modify extractant-metal ion interactions have been made and new tripodal phosphonate extractants have been prepared. Isolated liquid-liquid extraction complexes have been studied at the molecular level by spectroscopic and x-ray crystallographic methods. The resulting molecular architecture data have been used to design improved extractants and to model surface immobilized extractant-metal interactions. Extraction equilibria for several phosphonate extractants attached to polymer backbones and silica in contact with lanthanide and actinide ions have been obtained.

SRI International
Menlo Park, California 94025

408. Chemistry of Gaseous Lower-Valent Actinide Halides
D.L. Hildenbrand **$89,000**
Physical Sciences Division

The objective of this project is to provide accurate thermochemical information for key actinide halide, oxyhalide, and related systems, starting with uranium halides, so that the basic factors underlying the chemical bonding and chemical reactivity in these systems can be elucidated in a systematic way. Our principal focus is on the gaseous halides, mainly the lower-valent halides, since there is little or no thermodynamic or spectroscopic information on these species. Bond dissociation energy and absolute entropy data are derived from chemical equilibrium measurements made primarily by high temperature mass spectrometry. The bond dissociation energies and their variation with the number of halogen ligands yield insight into the electronic character of the bonding, while the absolute entropies provide useful checks on assigned structures and electronic partition functions. Current studies are concerned with the gaseous uranium-iodine and thorium-bromine systems, the lower-valent uranium oxyfluorides, the uranium chlorobromides, and the intermediate uranium fluoride solid phases. A clear pattern of bond dissociation energies is beginning to emerge; this pattern will be useful in modeling the thermochemistry of the heavier actinide halides, which will be much more difficult to study.

University of Tennessee
Knoxville, Tennessee 37996-1320

409. *Magnetic Measurements of the Transuranium Elements*

P.G. Huray **$97,000**
Department of Physics

A SQUID-based micromagnetic susceptometer in the facilities at the Transuranium Research Laboratory is being used to measure the magnetic properties of americium, curium, berkelium, californium, and einsteinium metals and compounds. The research catalogs magnetic behavior of unmeasured heavy actinides between 4.2 K and room temperature and 0 to 5 tesla. The study provides a measure of the degree of localization of the 5f electrons and examines the effects produced by neighbor-neighbor overlap. The effective magnetic moments of heavy atoms and the observed magnetic transition temperatures (if any) are examined within the context of the intermediate coupling model. Current work deals with the saturated moments of dhcp ^{249}Cf metal, monoclinic Cf_2O_3, fcc Cf_2O_3, Ba CfO_3, fcc ^{248}Cm metal, and the degree of magnetic order attained in the limit of low temperatures and high fields.

410. *Physical-Chemical Studies of the Transuranium Elements*

J.R. Peterson **$130,000**
Department of Chemistry

This project provides training for pre- and postdoctoral students in chemical research with the transuranium elements through continuing investigations of the basic chemical and physical properties of this group of elements and the interpretation and correlation of the results obtained. New knowledge is being accumulated in the following areas: (1) the role of the 5f electrons in the bonding in actinide elements and compounds; (2) the relationships of metallic structures to metallic valence and radius; (3) the extent and magnitude of the actinide contraction; (4) the magnetic, thermodynamic, spectroscopic, and crystallographic properties of these materials as related to general theories; (5) the effect of self-irradiation on chemical and physical properties; (6) the chemical and physical consequences of radioactive decay in the bulk-phase solid state; and (7) in general, the range of validity of the actinide hypothesis. Research activities include: (1) spectroelectrochemical studies in aqueous and nonaqueous media; (2) measurement of heats of solution; (3) absorption and Raman spectroscopies in solution and solid state (the latter as a function of temperature or pressure); (4) structural changes as a function of temperature or pressure; (5) direct or indirect (via radioactive decay) synthesis of compounds containing unusual oxidation states; (6) determination of the structures of einsteinium compounds; and (7) studies of the fundamental chemistries of the transeinsteinium elements.

Stanford Synchrotron Radiation Laboratory Operation

Stanford Synchrotron Radiation Laboratory
Stanford, California 94305

411. *Stanford Synchrotron Radiation Laboratory Operation*

A. Bienenstock **$6,900,000**

This project supports the Laboratory's operation, making possible otherwise-funded research by users in many scientitic areas. Research performed in the vacuum ultraviolet area includes: ionization properties of small molecules; structural and electronic properties of micro-structures; properties of ultra-thin layers and small clusters; kinetic process in laser materials; lithography and microscopy; and static properties and dynamic processes of chemisorbed gases. Research in the chemical and biological sciences includes: structure and function of homo- and heterogeneous catalysts; structure of metals; metal oxide and semiconductor surfaces and their interactions with small molecules; chemical reactivities in the gas phase; structure of general chemical compounds; multiple wavelength imaging; protein structures and functions; dynamics and fluctuations in biological systems; membrane structures and membrane-protein interactions; and structure and function of metal site in metalloproteins and metalloenzymes. X-ray physics and materials sciences research includes: structure of amorphous materials; coordination of impurities and alloying species; structures of, and phase transitions in, surfaces and thin surface layers; kinetics of structural changes in materials; phase transitions at high pressure; structure of crystalline materials; electronic structure of materials through edge absorption studies; fundamental x-ray scattering and absorption physics; and atomic physics. Development of advanced insertion devices for the enhancement of synchrotron radiation and of advanced instrumentation for the improved utilization of synchrotron radiation are also among the principal activities.

SPECIAL FACILITIES

The special facilities described on the following pages are supported wholly or partly by the Division of Chemical Sciences. They represent an assembly of unique and/or expensive equipment which would be costly to develop elsewhere. They represent research resources for the general scientific community, and qualified scientists from laboratories outside the host laboratory are encouraged to make use of them. However, any activity that can be carried out through commercially available laboratories is not appropriate for these DOE supported facilities.

The process by which an off-site scientist can use a facility is discussed in each facility summary. For the National Synchrotron Light Source and the Combustion Research Facility, see the section "User Mode." For the remaining facilities, see "Collaborative Use," which is a process based on the need for collaboration by the off-site scientist with one or more in-house staff members.

Each of the facility summaries also gives the names of individuals to contact for further information, a general description of the facility, and a list of technical data on the primary available instrumentation.

The Office of Basic Energy Sciences also supports other facilities not summarized here. Information concerning these can be obtained by contacting Dr. Louis C. Ianniello, Director of Materials Sciences, ER-13, U. S. Department of Energy, Washington, D.C. 20545.

ATOMIC SPECTROSCOPY FACILITY

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne spectroscopic facility is designed for high-resolution investigations of atomic and molecular optical spectra by using a unique combination of large-scale dispersive instruments with state-of-the-art holographic gratings and pulsed, sharply tunable coherent light sources for excitation energies of up to 11 eV. Photographic, Reticon array, and resonance-ionization detectors with associated data-processing equipment are available for a wide variety of experiments. Peripheral equipment includes a 50-kG superconducting magnet with a 24-inch room-temperature bore, and an automatic plate-measuring comparator. Nd-YAG laser-driven dye lasers are used with doublers and H_2-Raman scattering to cover the 200–850 nm range and to produce coherent radiation between 118 and 125 nm by four-wave mixing in mercury vapor.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

J. P. Hessler
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone:
Comm. (312) 972-3717
or FTS 972-3717

TECHNICAL DATA

Resolving power	
30-foot Paschen-Runge spectrograph	$>5 \times 10^5$
5-meter Czerny-Turner spectrograph	$>10^5$
Tunable dye lasers	$>10^6$
Vacuum-ultraviolet coherent source	$>10^7$
Wavelength range, nm	
30-foot Paschen-Runge spectrograph	200 to 900
5-meter Czerny-Turner spectrograph	120 to 500
Tunable dye lasers	200 to 850
Vacuum-ultraviolet coherent source	118 to 125

4.5-MV DYNAMITRON ACCELERATOR

Physics Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne Physics Division operates a high-current 4.5-MV Dynamitron accelerator which delivers magnetically analyzed beams of most atomic ions and many molecular ions. Among the unique facilities associated with the Dynamitron are (1) a beam line capable of providing "supercollimated" ion beams that permit angular measurements to accuracies of 0.1 mrad, (2) a beam-foil measurement system capable of measuring lifetimes to a few tenths of a nanosecond, (3) a 28-inch-diameter general-purpose scattering chamber, (4) a laser-ion beams system where an argon pumped dye laser beam is coaxial with the ion beam, (5) a variety of electron spectrometers including a high-resolution, large solid-angle McPherson spherical analyzer, and (6) a large area multiwire proportional counter capable of detecting up to eight particles simultaneously with submillimeter position and subnanosecond time resolution, and (7) a post-acceleration chopper system giving beam pulses with widths that can be varied from 1 nsec to several msec at repetition rates variable up to 8 MHz. PDP-11/45 and VAX 11/750 computer systems with direct links to Argonne's central computing facility are used for on-line data acquisition, analysis, and the control of experiments.

COLLABORATIVE USE

Visiting scientists use the accelerator either in collaboration with Argonne investigators or as independent groups.

PERSON TO CONTACT FOR INFORMATION

H. G. Berry
Physics Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone:
Comm. (312) 972-4039
or FTS 972-4039

TECHNICAL DATA

Range of terminal voltages attainable	0.3 to 4.5 MV
Range of ion beam currents attainable	0.1 nA to 500 μA
Monatomic singly charged ion beams available	Most elements
Monatomic multiply charged ion beams available	Rare gases, transition metals
Typical molecular-ion beams available	H_2^+, H_3^+, HeH^+, CH_n^+ ($n = 1,4$), OH_n^+ ($n = 1,3$), CO^+, O_2^+, etc.
Pulse mode (post-chopper)	
Pulse width	1 nsec to 10 msec
Repetition rate	1 MHz to 8 MHz

PREMIUM COAL SAMPLE PROGRAM

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The purpose of the Premium Coal Sample Program is to provide the coal science research community with long-term supplies of a small number of premium coal samples that can be used as standards for comparison. The premium coal samples produced from each coal and distributed through this program will be as chemically and physically identical as possible, will have well-characterized chemical and physical properties, and will be stable over long periods of time. Coals will be mined, transported, processed into the desired particle and sample sizes, and packaged in environments as free of oxygen as possible while maintaining the natural moisture content in order to ensure that the coals will be in as pristine and stable a condition as possible.

AVAILABILITY

Initial samples are expected to be available in mid-1985. Samples will be made available to research personnel at a nominal replacement cost. A very limited quantity of lump coal, stored under similar inert conditions, will be available on special request for special physical property measurements. Distribution of these samples will be guided by policies established with the help of a users advisory committee. The processing facility may be available for occasional processing of special samples.

PERSON TO CONTACT FOR INFORMATION

Dr. Karl S. Vorres
Chemistry Division, Bldg. 211
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

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Comm. (312) 972-7374
or FTS 972-7374
Telex:
TWX 910-258-3285
USDOE-CH ARGN

PULSE RADIOLYSIS FACILITY

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne linear electron accelerator was designed for chemical research. The moderate energy of the electron accelerator (maximum energies of 21 MeV transient mode, 14 MeV steady state) allows the use of the electron beam for the generation of transient species without nuclear activation. The pulse width can be varied from 25 psec to 10 μsec. In addition, a 5 psec pulse with the same peak current is presently being developed and is expected to be available by January, 1986. In liquids, transient concentrations up to 20 μ*M* can be generated with the 25-psec pulse, and concentrations in excess of 10 m*M* can be generated with the longest pulse. Instrumentation for measurement of chemical processes allows kinetic spectrophotometric absorption and emission and fast conductivity measurements. Simultaneous multiwavelength kinetic spectrophotometric measurements are possible, and very high time resolution measurements that use the short pulse capability of the linac can also be made, both in absorption and emission. All data acquisition equipment is computer interfaced to provide accurate data reduction. Sample preparation and handling facilities are available for solid, liquid, and gaseous samples.

COLLABORATIVE USE

Collaborative experiments can be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

Charles D. Jonah
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone:
Comm. (312) 972-3471
or FTS 972-3471

TECHNICAL DATA

Energy	
Transient mode	21 MeV
Steady-state mode	14 MeV
Pulse repetition rate	Single pulse, 800 pps (800 pps not possible for all pulses)
Current/pulse	
Transient mode	20 A
Steady-state mode	1.5 A
Picosecond pulse	25 nC
Pulse width	30 psec 4 to 100 nsec } transient mode 0.25 to 10 μsec } transient mode

ATOMIC PHYSICS AND NUCLEAR ANALYTICAL TECHNIQUES

Atomic and Applied Physics Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

The objective of this program is to make available facilities for research in atomic physics and the development and application of nuclear analytical techniques. Experiments in these fields require the availability of a wide range of ion and photon beams for maximum effectiveness. These beams cannot be provided at a single accelerator, but require the use of varied apparatus at a whole complex of accelerators. A 3.5-MV electrostatic accelerator is used primarily for experiments on nuclear analytical techniques. Notable features include a triton beam, medium resolution microprobe, rabbit system, and 200-kV ion implanter arranged for simultaneous implantation and analysis. The MP tandem accel-decel accelerator provides beams of most elements with an energy range from 2 MeV to 500 MeV. Ion charge state and ion energy can be selected over a wide range of energies using the accel-decel feature. Possible use of the tandem accelerators is determined by the needs of the relativistic heavy-ion program. Equipment for beam-foil spectroscopy and many types of ion-atom collision experiments are available. Photon beams with energies from 3 to 20 keV are provided at the National Synchrotron Light Source (NSLS). Either white or monochromatic radiation can be selected. The high brightness of the source gives unique opportunities in both atomic physics and nuclear analytical technique experiments. Extensive instrumentation is available in both areas.

COLLABORATIVE USE

These facilities are open for use by qualified scientists. Arrangements can be made for collaboration with Brookhaven scientists or for independent experiments. Proprietary use is possible on a full-cost recovery basis. In some cases a proposal for review by program advisory committees will be necessary.

PERSON TO CONTACT FOR INFORMATION

K. W. Jones
Division of Atomic and Applied Physics
Department of Applied Sciences
Building 901A
Brookhaven National Laboratory
Upton, NY 11973

Phone:
Comm. (516) 282-4588
or FTS 666-4588

TECHNICAL DATA

200-kV Ion Implanter	
Range of terminal voltages attainable	20 to 200 kV
Range of maximum ion beam currents available	1 to 100 μA
Ion beams available	Many elements
3.5-MV Electrostatic Accelerator	
Range of terminal voltages attainable	.3 to 3.5 MV
Range of maximum ion beam currents available	10 to 100 μA
Ion beams available	^1H, ^2H, ^3H, ^3He, ^4He, and heavier gaseous elements
Repetition rate	DC only
MP-TANDEM Accel-Decel Accelerators	
Range of terminal voltages available	1 to 18 MV
Output currents	Up to 1 μA
Ion beams available	Most elements
Ion energy and charge state	Variable with accel-decel capability
Repetition rate	DC or pulsed with variable repetition rate
NSLS X-Ray Facility	
Photon energy range	3 to 20 keV
Photon flux at target	$\sim 10^9$ photons/(μm^2–sec)

Photon flux at target —10^9 photons/(μm^2–sec)

NATIONAL SYNCHROTRON LIGHT SOURCE

National Synchrotron Light Source
Brookhaven National Laboratory
Upton, NY 11973

The National Synchrotron Light Source (NSLS) facility consists of a 750-MeV storage ring for VUV and IR research and a 2.5-GeV storage ring for X-ray research. Attractive features of the synchrotron radiation include high brightness and intensity, a broad and continuous spectral range, high polarization, and pulsed time structure (subnanosecond pulses). With each of the 28 X-ray and 16 VUV beam ports being further split into from 2 to 4 beam lines, it will be possible, when NSLS becomes fully operational, to have as many as 100 experiments running simultaneously. A 6-pole superconducting wiggler magnet and a 38-pole permanent magnet undulator have been constructed, and several wiggler and undulator magnets are presently being designed which will significantly increase the photon intensity and brightness.

The NSLS is a facility where a wide range of research techniques are being used by biologists, chemists, solid state physicists, metallurgists, and engineers for basic and applied studies. Among the techniques are EXAFS (extended X-ray absorption fine structure), scattering, diffraction, topography, radiography, fluorescence, interferometry, gas phase spectroscopy, photoemission, radiometry, lithography, microscopy, dichroism, and infrared vibrational spectroscopy.

USER MODE

The policy for experimental utilization of the NSLS is designed to enable the scientific community to cooperate in the design and fabrication of experimental apparatus. In addition to the beam lines constructed by the NSLS staff for general usage, a large number of beam lines have been designed and instrumented by Participating Research Teams (PRT's). The PRT's are given priority for up to 75% of their beam line(s) operational time for a three-year term. Research groups are now in the process of forming insertion device teams (IDT) to design and instrument beam lines and insertion devices.

General Users are able to perform experiments on an NSLS facility beam line or on a PRT beam line, which are available for use by non-PRT members for at least 25% of its total operational time. For the PRT beam lines, PRT's provide liaison and utilization support to General Users.

Proprietary research can be performed at the NSLS. A full-cost recovery fee will be charged for the amount of beam time utilized. The DOE has granted the NSLS a Class Waiver, under whose terms Proprietary Users of the NSLS will have the option to retain title to inventions that result from research performed at the NSLS.

A limited amount of funding is available to scientists from U. S. institutions of higher education under the NSLS–HFBR Faculty/Student Support Program. The program is designed to defray expenses incurred by faculty/student research groups performing experiments at the NSLS or at the HFBR. It is aimed at university users having only limited grant support for their research and will be used to support only the most deserving cases.

PERSON TO CONTACT FOR INFORMATION

R. Klaffky
NSLS, Bldg. 510E
Brookhaven National Laboratory
Upton, NY 11973

Phone:
Comm. (516) 282-4974
or FTS 666-4974

TECHNICAL DATA

Facilities	**Key features**	**Operating characteristics**
VUV electron storage ring	High brightness; continuous wavelength range ($\lambda > 5$ Å); 16 beam ports	0.75-GeV electron energy
X-ray electron storage ring	High brightness; continuous wavelength range ($\lambda > 0.5$ Å); 28 beam ports	2.5-GeV electron energy

Instruments	**Key features**
Monochromators	
Plane grating	12 Å $< \lambda <$ 1500 Å; high resolution
Zone plate	8 Å $< \lambda <$ 100 Å; moderate resolution
Toroidal grating	10 Å $< \lambda <$ 2500 Å; high intensity; moderate and high resolution
Extended range grasshopper	20 Å $< \lambda <$ 2000 Å; high resolution
Wadsworth	300 Å $< \lambda <$ 3000 Å; high intensity; moderate resolution
Seya and Czerny-Turner	1200 Å $< \lambda <$ 12000 Å; high intensity; moderate resolution
Two crystal	0.04 Å $< \lambda <$ 2500 Å; high resolution; fixed exit beam
Two crystal/two grating	2.5 Å $< \lambda <$ 2500 Å; high resolution; fixed exit beam
Six circle spectrometer/diffractometers	High positional and rotational accuracy
Experimental stations	Photoemission; magnetic circular dichroism; fluorescence; gas phase spectroscopy; microscopy; lithography; holography; EXAFS; inelastic scattering; crystallography; radiometry; topography; small angle scattering
Permanent magnet undulator	100 Å $< \lambda <$ 1000 Å; high intensity and brightness

JAMES R. MCDONALD LABORATORY

Department of Physics
Kansas State University
Manhattan, KS 66506

Three accelerators are operated primarily for atomic physics research. These accelerators are a 6-MV EN-tandem accelerator, a 3-MV Van de Graaff, and a 100-kV accelerator. Either foil or gas poststripping between the 90° and the switching magnet is possible for tandem beams. Available experimental facilities include (1) a 4.5-meter flight tube for impact parameter measurements, (2) a curved crystal X-ray spectrometer, (3) spherical sector and cylindrical electron spectrometers, (4) hydrogen atom and metal vapor oven targets, (5) low-energy high-charge recoil ion sources, (6) a 45-inch diameter scattering chamber, and (7) Si(Li), proportional counter, avalanche, and channel-plate detectors. The laboratory is available to users who require the unique facilities of the laboratory for experiments pertinent to DOE program goals.

COLLABORATIVE USE

Users are encouraged to seek a collaborator on the staff or can submit a brief proposal.

PERSON TO CONTACT FOR INFORMATION

Patrick Richard, Director
James R. McDonald Laboratory
Department of Physics
Kansas State University
Manhattan, KS 66506

Phone: (913) 532-6783

TECHNICAL DATA

EN Tandem

Beams	Most elements
Terminal voltages	0.3 to 6 MV
Output currents	Up to 10 μA, depending on the ion species and the charge state
Repetition rate	DC or 3-nsec pulses at rates up to 4 MHz
Magnet limitations	$ME/q^2 \leqslant 150$

3-MV Van de Graaff

Beams	^1H or ^4He
Terminal voltages	0.3 to 3 MV
Output currents	Up to 100 μA
Repetition rate	DC only
Magnet limitations	None

100-kV Accelerator

Beams	Most elements
Terminal voltages	20 to 100 kV
Output currents	Up to 10 μA, depending on the ion species
Magnet limitations	None

PULSE RADIOLYSIS FACILITY

Notre Dame Radiation Laboratory
University of Notre Dame
Notre Dame, IN 46556

The Notre Dame pulse radiolysis facility is based on a 5-nsec electron pulse from an 8-MeV linear accelerator. It is fully instrumented for computerized acquisition of optical and conductivity information on radiation chemical intermediates having lifetimes of 10 nsec and longer. Detectors having response times of ~2 nsec are available. For typical optical absorption studies, where one produces $10^{-5}M$ of intermediates, spectral and kinetic information can be obtained on species having extinction coefficients in excess of 100 $M^{-1}cm^{-1}$. Conductometric methods in aqueous solution cover the pH range of 3 to 11. Data are recorded digitally and stored in magnetically readable form for rapid off-line examination of spectral and kinetic details.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a proposal to the laboratory director.

PERSON TO CONTACT FOR INFORMATION

J. J. Bentley, Assistant Director
Notre Dame Radiation Laboratory
Notre Dame, IN 46556

Phone:
Comm. (219) 239-5362
or FTS 333-8220

TECHNICAL DATA

Electron source	8-MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	LSI-II
Pulse width	5, 10, 20, 50 nsec
Time resolution (RC)	2 nsec
Pulse current	Up to 1 A
Repetition frequency	0.2 sec^{-1}
Optical absorption measurements	
Spectral region	210 to 750 nm
Sensitivity	±0.00002 absorbance
Conductivity	
pH range	3 to 11
Sensitivity	±5 mhos/cm

ELECTROMAGNETIC ISOTOPE SEPARATIONS (CALUTRON) FACILITY

Operations Division
Oak Ridge National Laboratory
Oak Ridge, TN 37830

The objective of this facility is to separate and provide multigram quantities of highly enriched separated stable and selected radioactive isotopes, including the actinides, to the research community. An important aspect of the program is the research, development, and demonstration of cost-effective alternate methods of isotope enrichment as well as activities in ion source technology, beam dynamics, ion retention, and chemical recovery procedures. All isotopically enriched samples are distributed through a regular sales program or are circulated to the research community on a loan basis from the Research Materials Collection, administered under the direction of DOE. The program is responsible for the production, distribution, quality control, and reprocessing of the material in the Research Materials Collection. Applications for the loan of samples from this collection for nondestructive research projects germane to DOE programmatic interests are received at any time.

PERSON TO CONTACT FOR INFORMATION

J. G. Tracy
Stable Isotope Enrichment
Operations Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37831

Phone:
Comm. (615) 574-0425
or FTS 624-0425

EN-TANDEM

Physics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The EN-Tandem is operated primarily as an atomic physics facility. The highest terminal voltage is 6.5 MV. The widest possible variety of ion species are available from a selection of ion sources. Two 90° magnets with a stripper (gas or foil) between them follow the accelerator so that a range of charge states is available for any ion at a given energy. Available facilities include (1) a merged electron–heavy ion beam apparatus with a merged region ~1 meter in length; (2) an ~14-meter flight tube with the capability of doing very small angle scattering and detecting individual charge states; (3) a Penning ion trap apparatus; (4) an Elbeck magnetic spectrograph with position sensitive detectors; (5) Si(Li) detectors and a curved crystal spectrometer; (6) both low- (eV to keV) and high- (MeV) monoenergetic positron sources (being developed); (7) data acquisition and analysis is performed using a CAMAC based VAX-11/750 computer system.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a research proposal to the EN-Tandem manager.

PERSON TO CONTACT FOR INFORMATION

P. D. Miller
Bldg. 5500
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37831

Phone:
Comm. (615) 574-4781
or FTS 624-4781

TECHNICAL DATA

Beams	Most elements
Terminal voltages	0.3 to 6.5 MV
Source beam currents	Several hundred nA to several μA
Output currents	Up to 2 μA, depending on the ion species and charge state
Repetition rate	DC only
Magnet limitations	$ME/q^2 \leq 80$

HIGH FLUX ISOTOPE REACTOR

Operations Division
Oak Ridge National Laboratory
Oak Ridge, TN 37830

The prime purpose of the High Flux Isotope Reactor (HFIR) is to make research quantities of ^{252}Cf and other transuranium isotopes. These materials are produced in the flux trap in the center of the HFIR fuel element where a thermal-neutron flux of 3×10^{15} neutrons/(cm^2 · sec) is available to irradiate the curium target material. The HFIR is a beryllium-reflected light-water-cooled and -moderated, flux-trap reactor with a design power level of 100 MW. It burns 93% enriched ^{235}U fuel in aluminum-clad plates. Additional irradiation facilities are provided in the beryllium reflector around the fuel element to increase the production rate of the heavy isotopes.

The HFIR also has, as a secondary purpose, the performance of diverse irradiations, tests, and experiments which benefit from the exceptionally high neutron flux available. In the fuel element flux trap, a hydraulic-rabbit tube provides access to the maximum thermal-neutron flux in the reactor for short-term irradiations, and other positions are ideal for fast-neutron irradiation-damage studies. The beryllium reflector contains numerous experiment facilities with thermal-neutron fluxes up to 1×10^{15} neutrons/(cm^2 · sec). These facilities can accommodate static experimental capsules, complex fuel-testing engineering loops, and special experimental isotope irradiations, the targets for which are prepared by the Oak Ridge National Laboratory Isotopes Group. Four beam tubes are used for neutron-diffraction experiments and a small-angle neutron scattering facility sponsored by the National Science Foundation is available for use by researchers from universities, industry, and other national laboratories.

PERSON TO CONTACT FOR INFORMATION

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Oak Ridge, TN 37831

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TRANSURANIUM PROCESSING PLANT

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37830

The objective of this program is to supply transplutonium elements for use in research. This involves operation of the Transuranium Processing Plant (TRU), which is the production, storage, and distribution center for the DOE heavy-element research program. Target rods are fabricated at TRU, irradiated in the High Flux Isotope Reactor (HFIR), and processed at TRU for separation, recovery, and purification of the heavy actinides up through ^{257}Fm. Since their construction in the mid-1960's, TRU and HFIR have provided the western world's supply of elements beyond curium (atomic number 96), either directly or by furnishing starting materials for further nuclear-synthesis reactions. The transuranium element isotopes produced in TRU are used nationally and internationally to study the basic physics and chemistry of the transuranium elements and, also, they are being used in research and development programs relating to environmental effects, biological effects, and waste isolation.

PERSON TO CONTACT FOR INFORMATION

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COMBUSTION RESEARCH FACILITY

Combustion Sciences Directorate
Sandia National Laboratories, Livermore
Livermore, CA 94550

Current activities at the Combustion Research Facility (CRF) supported by the Division of Chemical Sciences emphasize the development and the applications of new diagnostic techniques to the study of basic flame processes, as well as research in fundamental chemistry important in combustion. (These programs are individually described elsewhere in this publication). In addition, DOE/Conservation sponsors programs at the CRF in combustion technologies, and DOE/Fossil supports programs in coal combustion and related diagnostics development.

Complete facilities for resident and visiting researchers are available: offices for 60 staff, a meeting room accommodating 250 people, a laboratory building housing 14 independent experiments, special facility laser systems, a dedicated VAX computer, and access to a Cray computer.

The facility is located in Livermore, California, in the San Francisco Bay area, near major universities and other U. S. Government supported laboratories.

USER MODE

Qualified scientists are encouraged to take advantage of the specialized resources available at CRF. Prospective participants should submit a brief proposal to the laboratory director. Criteria for selection include technical merit, the extent to which CRF facilities are used, overlap with DOE program objectives, and the availability of specific equipment.

In general, the CRF will host visiting scientists to use the special-purpose lasers, work with resident staff, make use of computers and codes, and set up experiments. Visitors pay for their own salary, travel, housing, meals, and other local expenses. Facility lasers, apparatus, technicians, instrumentation, computers, and support-group services are provided without charge for research that is not proprietary. Research results from nonproprietary projects are expected to be published and disseminated.

For scientists with active government contracts, support for CRF research often can be arranged on an informal basis with the contract manager. There are opportunities for faculty, postdoctoral scientists, and graduate students to obtain Sandia support for combustion-related research at CRF.

In specific instances, proprietary research can be carried out at CRF. For this type of work, the DOE will be reimbursed on a full cost recovery basis for the use of all CRF resources. Details of a DOE Class Waiver for patent rights are available.

PERSONS TO CONTACT FOR INFORMATION

Dan L. Hartley, Director
Combustion Research Facility
Sandia National Laboratory
Livermore, CA 94550

Phone:
Comm. (415) 422-2747
or FTS 532-2747

or

Peter L. Mattern, Manager
Combustion Sciences Department
Sandia National Laboratory
Livermore, CA 94550

Phone:
Comm. (415) 422-2520
or FTS 532-2520

TECHNICAL DATA

Equipment	Key features
Flashlamp-pumped, tunable dye laser	Long pulse, high energy, high average power: 2-μsec pulse length 5 J/pulse, 10 Hz Tunable 440 to 620 nm 0.03-nm bandwidth
Multipurpose pulsed laser system	High peak power, high resolution doubled YAG and tunable dye lasers: Single mode capability 10 to 500 mJ/pulse 10 to 20 nsec/pulse
Low-pressure flames	10 μ to 1 atm Mass spectrometer sampling probe
Atmospheric flames	Diffusion and premixed flames
High-pressure flame	Combination of diffusion flame burner with high pressure flow chamber: Pressures up to 20 atm Slot-geometry burner 2-0 laminar diffusion
Vertical turbulent diffusion flame	Open-circuit, induced-draft wind tunnel with co-flowing axisymmetric fuel jet: 30- by 180-cm viewing section to 6000 scfm flow
Atmospheric Combustion Exhaust Simulator (ACES)	Atmospheric pressure combustion exhaust chamber: To 1200°C 0.5 to 100 m/sec flow speed Trace species and particulates Optical and physical probes Materials test section
Combustion bomb	Simulates constant-volume engine combustion
Internal combustion research engines	Highly repeatable environment for homogeneous charge and diesel combustion studies
Experimental diagnostics research facilities	Laser fluorescence laboratory

Equipment	Key features
	Coherent Raman spectroscopy laboratories
	Laboratory for laser ionization, saturation, optogalvanic detection of trace species
	Kinetics laboratories with tunable quasi-cw UV and ring dye lasers for analysis; excimer lasers for photolysis
Computing facilities	Minicomputers in laboratories Access to CRF VAX 11/780 Access to Sandia National Laboratory, Livermore, CRAY via in-house staff

STANFORD SYNCHROTRON RADIATION LABORATORY

Stanford Synchrotron Radiation Laboratory
Bin 69, P.O. Box 4349
Stanford, CA 94305

SSRL is a national facility for the utilization of synchrotron radiation in materials sciences, biology, chemistry, physics, medical science and other disciplines. In addition to scientific research using synchrotron radiation the Laboratory program includes the development of advanced sources of synchrotron radiation (e.g., insertion devices for the enhancement of synchrotron radiation, new ring designs) and the development of state of the art instrumentation for the use of synchrotron radiation. The radiation comes from the 4 GeV storage ring, SPEAR, a SLAC facility originally built for high energy physics research. SPEAR is dedicated to the production of synchrotron radiation half of its operating time. Presently SSRL has 19 experimental stations on 7 beam lines covering the spectrum from 6 to 45,000 eV. An undulator beam line serving three experimental stations covering the energy range 10 to 1,000 eV is in the commissioning stage. Under construction is an undulator beam line on the storage ring PEP which will provide the world's brightest photon beam at x-ray wavelengths.

USER MODE

SSRL is currently used by approximately 550 scientists from 108 institutions in 32 states and 11 foreign countries. Access to the facility is through a refereed proposal system. Proposals are due September 1 and March 1 each year. The booklet "General Information and Proposal Guidelines" available from SSRL contains information pertinent to proposal submittal. To date 953 proposals for research have been received. Demand for experimental time is approximately twice that which can be accommodated.

PERSON TO CONTACT FOR INFORMATION

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Comm. (415) 854-3000, ext. 3191
or FTS 461-9300, ext. 3191

TECHNICAL DATA

CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS

	Horizontal Angular Acceptance (Mrad)	Energy Range (eV)	Resolution	Approximate Spot Size Hgt × Wdth (mm)	Remarks
Beam Line I					
1-1 (4°)	2.0	32–1000	$\Delta\lambda = .1\text{-}.2\text{Å}$	2.0 × 1.0	Double Focus
1-2 (8°)	4.0	4–40	$\Delta\lambda = .2\text{-}6\text{Å}$	1.0 × 3.0	Highly Polarized Double Focus
1-4 (Curved Crystal)	2.2	6000–9500	~60 eV	0.25 × 0.5	Double Focus Scattering
1-5 (EXAFS I)	1.0	3800–29300	$\Delta E/E \sim 10^{-4}$	2.0 × 20.0	Rapidly Tunable Unfocused
Beam Line II					
II-2	4.8	2800–8900	$\Delta E/E \sim 5 \times 10^{-4}$	2.0 × 4.0	Rapidly Tunable Focused
II-3	1.0	2800–30000	$\Delta E/E \sim 5 \times 10^{-4}$	2.0 × 20.0	Rapidly Tunable Unfocused
II-4	1.0	3200–30000	White Radiation	4.0 × 15.0	
Beam Line III					
III-1 (4°)	2.0	15–1200	$\Delta\lambda = .05\text{-}2\text{Å}$	1.0 × 1.0	Double Focus
III-3 (2°)	8–10	800–4000	0.35–7 eV	20 × 4.0	Ultra High Vacuum
III-4 (3°)	2.0	2–3000	White or $\Delta\lambda/\lambda = .01$	2 × 8	Differentially Pumped
Beam Line IV (Wiggler)					
IV-2	1.0	2800–45000	$\Delta E/E \sim 10^{-4}$	2.0 × 20.0	Rapidly Tunable Unfocused
	2.3	2800–22000	$\Delta E/E \sim 5 \times 10^{-4}$	2.0 × 6.0	Rapidly Tunable Focused
IV-3 & IV-1	1.0	2800–45000	$\Delta E/E \sim 10^{-4}$	2.0 × 20.0	Rapidly Tunable Unfocused
Beam Line VI (Wiggler)					
VI-2	1.0	2800–45000	$\Delta E/E \sim 10^{-4}$	2.0 × 20.0	Rapidly Tunable Unfocused
	3.0	2800–21000	$\Delta E/E \sim 5 \times 10^{-4}$	2.0 × 6.0	Rapidly Tunable Focused
Beam Line VII (Wiggler)					
VII-1 (Rotation Camera)	1.0	4500–8500	$\Delta E/E \sim 8 \times 10^{-4}$	0.6 × 3.0	Double Focus
VII-2	1.0	2800–45000	$\Delta E/E \sim 10^{-4}$	2.0 × 20.0	Rapidly Tunable Unfocused
	4.6	2800–10200	$\Delta E/E \sim 5 \times 10^{-4}$	2.0 × 6.0	Rapidly Tunable Focused
VII-3	1.0	2800–45000	$\Delta E/E \sim 10^{-4}$	2.0 × 20.0	Rapidly Tunable
Beam Line 0-0					
(Lifetimes Port)	1.8	1–6	Bandpass ≥ 10Å	4.0 × .4	Pulsed Visible Light

January 1985

FY 1985 EQUIPMENT FUNDS

Outlay funds of the Office of Basic Energy Sciences are divided among operating, equipment, and construction funds. Equipment funds are provided primarily to DOE laboratories. (Operating funds provided to other contractors are used for all costs, including purchase of necessary equipment.) FY 1985 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	Equipment funds
Ames Laboratory	$ 455,000
Argonne National Laboratory	1,635,000
Brookhaven National Laboratory	1,302,000
Idaho National Engineering Laboratory	14,000
Lawrence Berkeley Laboratory	711,000
Lawrence Livermore National Laboratory	5,000
Los Alamos National Laboratory	$ 56,000
Monsanto Research Corporation–Mound	81,000
National Institute for Petroleum and Energy Research	20,000
Notre Dame Radiation Laboratory	333,000
Oak Ridge National Laboratory	955,000
Pacific Northwest Laboratory	157,000
Pittsburgh Energy Technology Center	10,000
Sandia National Laboratories, Albuquerque	60,000
Sandia National Laboratories, Livermore	700,000
Solar Energy Research Institute	96,000
Stanford Synchrotron Radiation Laboratory	780,000

INSTITUTION INDEX

SELECTED TOPICS OF GENERAL INTEREST

o = onsite list
— = off " "

INVESTIGATOR INDEX

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