

Summaries of FY 1981 Research in the Chemical Sciences

August 1981

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

Printed in the United States of America

Available from

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes

Printed Copy:	\$21.50
Microfiche Copy:	\$ 3.50



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U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences
Washington, D.C. 20545

PREFACE

The purpose of this booklet is to help 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.

Chemists, physicists, chemical engineers and others who are considering the possibility of proposing research for support by this Division will find the booklet useful for gauging the scope of the program in basic research, and the relationship of their interests to the overall program. These summaries are intended to provide a rapid means for becoming acquainted with the Chemical Sciences program to members of the scientific and technological public and interested persons in the Legislative and Executive Branches of the Government. Areas of research supported by the Division are to be seen in the section headings, the index and the summaries themselves. Energy technologies which may be advanced by use of the basic knowledge discovered in this program can be seen in the index and again (by reference) in the summaries.

The research program 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 Chemical Sciences. Another important consideration is the emphasizing of chemical, physical and chemical engineering subdisciplines which are advancing in ways which produce new information related to energy, needed energy data, or new ideas. Another consideration concerns the varying levels of knowledge needed by the different developing energy technologies.

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, or teaching responsibilities. Thus, about 70% of the funding goes to Federal laboratories, 25% goes to the academic sector, and the remainder is at industrial and not-for-profit laboratories.

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 booklet). Other questions about the program may be directed to the undersigned.

A handwritten signature in black ink, appearing to read "Elliot S. Pierce". The signature is written in a cursive style with a large initial "E" and "P".

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

Chemical Sciences Division
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Department of Energy
Washington, D.C. 20545

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Each Branch of the Division of Chemical Sciences is divided into programs which cover various disciplines. The following is a description of each of those programs. The staff members responsible for each program are indicated on page iii.

FUNDAMENTAL INTERACTIONS BRANCH (01-)

Photochemical and Radiation Sciences (01-01)

This program consists of research into the interactions of radiation with matter in all forms, but particularly with gases and liquids. A large part deals with the effects of ionizing radiation and fast electrons. The photochemical research is largely devoted 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 homo- and heterogeneous media, photoelectrochemistry, photocatalysis, and the molecular storage of energy. 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 will be centered at the National Synchrotron Light Source at Brookhaven National Laboratory.

Chemical Physics (01-02)

Disciplines covered by this program include chemical dynamics, energy transfer, molecular structure and spectroscopy, theoretical quantum chemistry, and statistical mechanics.

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 (01-03)

The Atomic Physics Program supports basic research on phenomena concerning atoms and their ions. Support is provided for experimental and theoretical studies of atom and ion structures, energy levels and energy state lifetimes, and of transport and exchange processes characterized by the rate at which transfer of energy, momentum or matter occurs. These studies strive to attain the best and most complete knowledge of the properties and interactions of photons, electrons, atoms, ions and simple molecules.

Recent emphasis of this research has been on the understanding of relatively high energy atomic physics that involves (1) ions stripped of all or most of their electrons, and (2) atoms and ions whose electrons are promoted in energy up to and including the energy continuum.

PROCESSES AND TECHNIQUES BRANCH (02-)

Chemical Energy (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 characterization and transformation of fossil resources - particularly coal, (3) the conversion of biomass and related cellulosic wastes and (4) hydrogen production and storage. The disciplines of organic, bio-, inorganic, physical, thermo- and electrochemistry, including the more chemically oriented chemical engineering, 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 (02-02)

This program is directed at improving our basic understanding of methods for separating mixtures of gases, liquids, solids and their component molecules, cations, anions, and isotopes. A substantial part of the program involves research aimed at discovering the relationship between the structure of organic extractant molecules and their selectivity for cations, anions and their complexes as used in solvent extraction. The isotope separation program emphasizes isotopic properties and isotope effects and is quite basic.

Analysis (02-03)

The analytical program is aimed at supporting research on analytical techniques where a better understanding of basics would enable other investigators to improve the sensitivity, reliability, ease of operation and/or lower the costs of analytical determinations. Entirely new analytical techniques are also investigated but this program is not an instrument development program. New techniques are quickly reported in the literature so that those interested in instrument development can build on work supported by this program. The program covers optical spectroscopy, mass spectroscopy, photoacoustic spectroscopy, particle spectroscopy, laser spectroscopy, activation analysis, and many other areas of analytical chemistry. In other words, this program is not geared to using existing techniques to unravel the composition of materials nor to develop techniques to analyze particular species, but is aimed at obtaining a thorough understanding of all of the various aspects of chemical analysis so that others may use this understanding to improve the uses of analysis.

Chemical Engineering Sciences (02-04)

This program addresses the more scientific and energy-related aspects of such engineering topics as fluid and particle dynamics, mass transport, thermodynamics and physical and chemical rate processes. Particular attention is given to turbulence research related to combustion; experimental and theoretical thermochemical and thermophysical properties, especially on mixtures, and phase equilibria, including supercritical extraction phenomena; research on gas-solid reaction modeling; and transport through porous media. Emphasis is given to improving and/or developing the scientific base for engineering generalizations and their unifying theories.

The following is a list of "persons in charge" of Chemical Sciences projects at DOE laboratories. These individuals are department/division, or laboratory administrators who can provide information about specific programs or refer inquiries to appropriate individuals.

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Laboratory Project Data

All the summaries of projects funded by a particular Chemical Sciences program (e.g., chemical physics) in a particular Laboratory's division or department are in a contiguous sequence in this book. Total dollars for each such sequence are given at its beginning.

There are two numbers above each summary, other than its entry number. The number immediately to the right of the project title indicates the scientific person years devoted to the project. The other number is the four digit code which identifies the Chemical Sciences program which funds the project, as defined previously.

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total \$255,000

- | | | | |
|----|---|-----|-------|
| 1. | PHOTOPHYSICS, PHOTOCHEMISTRY AND
SPECTROSCOPY
G. J. Small | 3.0 | 01-01 |
|----|---|-----|-------|

This program has as its general goal an understanding of mechanisms by which vibronically excited states of organic molecules and solids are created by linear and nonlinear interactions with photons, and the subsequent excited state relaxation processes, both photophysical and photochemical. Specific current problems include: the structure of and photoisomerization processes in amorphous solids and their probing with hole burning and fluorescence line narrowing spectroscopy; the role of mixed exciton-photon states (polaritons) in light absorption and their generation in crystals; utilization of jet cooled excitation and fluorescence spectroscopy for the study of charge-transfer states and vibrational relaxation in isolated molecules; electronic energy transport in ordered and disordered solids and; the application of coherent Raman spectroscopies to the problem of vibrational relaxation in molecular glasses.

- | | | | |
|----|--|-----|-------|
| 2. | PICOSECOND SPECTROSCOPY AND REACTION
DYNAMICS
W. S. Struve | 3.0 | 01-01 |
|----|--|-----|-------|

This program emphasizes applications of picosecond lasers to studies of photochemical mechanisms and time-resolved photocurrents in electrochemical cells. Gas-phase and solution-phase photodissociation of aryl iodides is probed by picosecond-resolved fluorescence and transient absorption experiments, and contrasted with the known relaxation dynamics of the aryl substrate. Similar studies are directed to charge transfer photochemistry of organic carbanions in solution. Solvent effects on the competition between predissociation and vibrational relaxation in halogen diatoms are monitored using fluorescence spectra and profiles under tunable picosecond pumping. This research is oriented toward an improved understanding of excited state processes pertinent to solar photochemistry.

Photochemical and Radiation Sciences

Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Total \$3,300,000

3. RADIATION CHEMISTRY OF LIQUIDS, SOLUTIONS AND ORGANIC COMPOUNDS 4.0 01-01
G. Closs, C. Jonah, J. Miller,
M. Sauer, S. Gordon, A. Trifunac,
K. Schmidt

This research has two goals, to understand the mechanisms of energy deposition in polar and nonpolar liquids and to use the reactive species formed by primary events as reagents and probes to study problems of fundamental interest. The structure and reactivity of primary species formed in organic solvents give information about these unusual chemical species. Solvation and reaction rates of solvated electrons are useful probes to energy deposition in polar media. The species created by radiation are probes for studying electron transfer, redox processes, free radicals and excited states in both polar and nonpolar media. Organic radicals such as tropilium ions and cyclopropenyl radicals are being studied to understand their structure and aromaticity. The redox chemistry and hydrolysis mechanisms of actinides are being studied to understand the role of f electron structure and the chemical processes which occur in nuclear waste management. Yields of radicals using high LET particles are being studied. The basic tools being used are the ANL picosecond electron linac and 3 MeV Van de Graaff.

4. PREPARATION OF ORGANISMS AND BIOLOGICAL MATERIALS OF UNUSUAL ISOTOPIC COMPOSITION 2.0 01-01
H. Crespi, J. J. Katz, J. Norris

This program has as its objective the production of photosynthetic and other organisms substituted with biologically important stable isotopes such as ^2H , ^{13}C , ^{15}N and ^{25}Mg . A large number of green algae, blue-green algae, bacteria, yeasts and molds is routinely available in unnatural isotopic composition involving single or multiple substitution. Isotopically altered materials are necessary to the full application of electron spin echo spectroscopy, electron spin resonance and nuclear magnetic resonance spectroscopy, small-angle neutron scattering analysis, and resonance Raman spectroscopy to problems in photosynthesis. Isotopically altered green and blue-green algae, photosynthetic bacteria and Halobacterium halobium are cultured on a large scale for the support of photosynthesis studies. In addition, effort is directed toward the efficient preparation of large amounts of chlorophyll and its derivatives for use in biomimetic studies. A research effort is centered about the structure and function of bacteriorhodopsin, the light-driven, proton pumping membrane protein of the Halobium species of bacteria.

Chemistry Division, ANL, continued

5. GAS PHASE RADIATION CHEMISTRY RELEVANT TO COMBUSTION AND ATMOSPHERIC REACTIONS 3.0 01-01
S. Gordon, M. Sauer, C. Jonah,
W. Mulac

The goals of this research are to measure and understand the fundamental parameters relevant to the reactions of reactive species involved in atmospheric and combustion chemistry. The experimental work includes the determination of the rate constants of reactions involving OH, HO₂ and O. Absorption spectrophotometry in conjunction with pulse radiolysis is used to follow reactant or product concentrations as a function of time. Extension of the temperature range to at least 1000 K is underway because of the importance of the higher temperature domain to combustion chemistry. An advantage of the pulse-radiolysis technique is that reactions can be examined at higher pressures than is convenient using other techniques, thereby facilitating determination of third-body effects.

6. CHLOROPHYLL AND PHOTOSYNTHESIS RESEARCH 5.0 01-01
J. J. Katz, J. C. Hindman

Physical and chemical studies of laboratory model systems and of photosynthesis in vivo are in progress to clarify chlorophyll function in the primary light conversion events of photosynthesis. Laser photochemistry techniques are being used (a) to establish the excited state properties of chlorophyll; (b) to examine the effect of excitation frequency on in vivo fluorescence; and (c) to study energy transfer in model systems containing defined chlorophyll species. The primary objective in these studies is an assignment of the fluorescence emissions of photosynthetic organisms in terms of specific chlorophyll species. Model systems (especially for bacteriochlorophyll) for more complete photoreaction centers and for antenna chlorophyll are being prepared by (a) self-assembly and (b) chemical syntheses involving allomerization reactions. Plasma desorption mass spectroscopy and the nmr spectroscopy of immobilized chlorophyll systems are being developed to characterize the stoichiometry and structures of chlorophyll model systems of interest.

Chemistry Division, ANL, continued

7. ELECTRON TRANSFER PROCESSES STUDIED BY RADIATION CHEMISTRY AND PHOTOCHEMISTRY 4.6 01-01
J. Miller, G. Closs, D. Meisel,
C. Jonah

This program studies basic principles for photochemical energy conversion and storage. These include electron transfer by excited states of molecules, suppression of back reactions of energy-rich intermediates, and redox catalysis to convert these reactive intermediates into useful fuels. Pulse radiolysis, laser flash photolysis, fluorescence spectroscopy, dynamic nuclear spin polarization and single-photon counting are being used to measure: (1) distances possible for an initial charge separation step; (2) control of long-distance electron transfer rates by the nature of the molecules between the donor and acceptor; (3) enhancement of charge separation efficiency by increasing charge density in functionalized polymers; (4) efficiencies of colloidal metal catalysts for hydrogen production from water, including their comparison to bulk electrodes; and (5) structures of short-lived ion pairs in solution. Fundamental understanding from these studies will enable synthesis by design of efficient molecular charge separation machines, and effective redox catalysts for capture of light energy as usable fuels.

8. PHOTOSYNTHESIS STUDIES: REACTION CENTER STRUCTURES, FUNCTIONS AND MECHANISMS 4.4 01-01
J. Norris, G. Closs, L. Shipman,
M. Wasielewski, M. Thurnauer,
M. Bowman

The fundamental goal of this program is the development of artificial photosynthesis through the better understanding of the natural photosynthetic unit. The work emphasizes the investigation of structural features of photosynthesis related to the mechanisms of photoinduced electron transfer reactions that occur in the picosecond to nanosecond time domain. Structure and mechanisms are probed by a variety of means, including theory, optical spectroscopy, unnatural isotope biology, and especially magnetic resonance. Specific areas that are under investigation include the following: (a) determination of accurate distances between members of the electron transport chain; (b) measurement of relative angles of orientation between various components; (c) identification of new long- and short-lived photoactive intermediates, particularly in green plants; (d) establishment of the kinetics of electron transfer in the initial chemical steps of photosynthesis; and (e) development of new theoretical insight to energy transduction and the structure of the photosynthetic machinery.

Chemistry Division, ANL, continued

9. RADIATION AND PHOTOCHEMISTRY STUDIED BY MAGNETIC RESONANCE 4.2 01-01
A. D. Trifunac, G. Closs

Magnetic resonance methods are being developed and applied to the study of fast chemical processes in radiation and photochemistry. Several methods involving electron paramagnetic and nuclear magnetic resonance of liquids and solids are being utilized to detect and study transients in pulse radiolysis and laser photolysis. Studies now in progress include quantitative study of kinetics, electron spin relaxation, and electron and nuclear spin polarization of transient radicals and their reaction products. These studies are aimed at providing better understanding of the interaction between the reactive radicals in solution and in exploring the possibilities of influencing their chemistry by application of magnetic fields. Excited states produced in pulse radiolysis and by laser-induced photoionization are being studied by optically detected electron paramagnetic resonance. These processes involving charge separation and recombination are of fundamental importance in any scheme of energy storage. A new solid state NMR spectrometer will be used to study pulse radiation damage in polymers.

10. ARTIFICIAL PHOTOSYNTHESIS 2.2 01-01
M. Wasielewski

Artificial photosynthesis research is directed toward the laboratory duplication of natural photosynthetic solar energy conversion. Synthetic photoreaction centers are being prepared as models of their natural counterparts. These models include novel monomeric chlorophyll enol electron donors and complex donor-acceptor systems. The latter models place chlorophyll electron donors in fixed geometries relative to both pheophytin and quinone electron acceptors. Time-resolved optical absorption and emission spectra of the models are being examined for evidence of light-induced charge separation. The radical ions of the various oxidized donors and reduced acceptors are being prepared electrochemically and characterized by their optical and magnetic resonance properties. Experiments utilizing the model systems in a prototype biomimetic device, a synthetic leaf, are being pursued. These studies involve using thin films of photoreaction center models to photocatalyze chemical reactions that are energy intensive.

Photochemical and Radiation Sciences

Chemistry Department
 Brookhaven National Laboratory
 Upton, New York 11973

Total \$2,908,000

- | | | |
|---|-----|-------|
| 11. RADIATION CHEMISTRY | 5.3 | 01-01 |
| B. H. J. Bielski, R. W. Dodson,
R. A. Holroyd, H. A. Schwarz | | |

This program uses radiolysis and photolysis, emphasizing pulse methods, to study the behavior and reactions of transient chemical species (ions, electrons, free radicals, and excited states of molecules). Principal areas of investigation are: properties and reactions of electrons in dielectric fluids, reactions of superoxide radicals and singlet oxygen in biological systems, reactive metal ion intermediates in redox reactions, and electron transfer reactions in photosynthesis. The aims of the program are to provide the basic knowledge needed for the understanding and control of chemical reactions involving transient species, many of which are components of energy production processes (direct solar conversion, combustion, etc.) or are harmful consequences of these same processes (corrosion, environmental pollution, etc).

- | | | |
|---------------------------------------|-----|-------|
| 12. SELECTIVE LASER-INDUCED CHEMISTRY | 2.5 | 01-01 |
| D. M. Brenner | | |

The research program in laser photochemistry and spectroscopy currently involves experiments related to the phenomenon of infrared multiphoton absorption and subsequent chemistry. The objective of these experiments is to reveal the dynamics of absorption by probing the internal energy distribution of vibrationally-excited molecules prior to reaction. These measurements involve energy transfer, spectroscopy, product analysis and opto-acoustic studies. This wide range of experiments permits an investigation of the exceedingly complex nature of IR multiphoton-induced chemistry from several different perspectives. A knowledge of the partitioning of excess energy in photodissociation reactions is fundamental to an understanding of chemical dynamics and energy storage. In particular, some photolytic reactions involve, in part, the conversion of light into vibrationally excited products. The details of this energy transformation are being examined in the laboratory with several techniques including laser-induced fluorescence, photoionization, and infrared chemiluminescence.

Chemistry Department, BNL, continued

13. PHOTOCHEMICAL ENERGY CONVERSION
C. Creutz, N. Sutin

6.2

01-01

This program involves photochemical investigations of transition metal complexes and, in particular, the electron-transfer properties of charge-transfer excited states. Particular attention is being paid to systems capable of effecting the decomposition of water into hydrogen or other useful chemicals and oxygen. 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 of this program is the quantitative study of these physical and chemical deactivation processes; the lifetimes and other physical properties of excited states are being measured and the rates of electron-transfer reactions of transition metal complexes are being determined. An additional direction of the program involves investigations of useful thermal reactions of transition metal ions in very high and very low oxidation states.

14. PICOSECOND SPECTROSCOPY
T. L. Netzel

2.5

01-01

Photochemistry can be divided into two classifications: unimolecular primary processes usually occurring on a sub-nanosecond time scale, and dark reactions which may be multi-molecular and occur on a longer time scale. This research program is designed to investigate the ultrafast unimolecular processes in complex molecular structures such as cofacial diporphyrins, covalently linked two- and three-membered chlorophyll aggregates, and inorganic compounds with two metal nuclei. The major experimental technique is picosecond absorption spectroscopy and the scientific focus is on understanding light-driven electron transfer processes. This theme is present in each of the study areas: diporphyrin and polychlorophyll molecules as well as polynuclear metal complexes. However, these processes must be viewed in the context of a broad understanding of early excited state photophysics. This is especially true for transition metal complexes.

Chemistry Department, BNL, continued

15. CHEMISTRY RESEARCH AT THE NSLS	6.3	01-01
M. D. Newton, Coordinator	1.6	02-01

In this program, the aim is to advance a number of areas of chemical research by utilization of photon beams from the National Synchrotron Light Source (NSLS), which is to begin first operations at Brookhaven in the summer of 1981. NSLS will provide high intensity, pulsed, polarized photon beams ranging in energy from the ultraviolet to the x-ray region. Crucial to the research is the quality of the experimental facilities to be available, and members of the Chemistry Department have been active in designing and building some of the lines that they and colleagues elsewhere will use. Problems to be pursued at the NSLS are in many cases outgrowths of on-going Departmental work and include gas phase photoionization and chemical kinetics studies, fluorescence lifetime and photoconductivity measurements, photoelectron spectroscopy, and x-ray diffraction. Experiments are also being planned on the EXAFS and x-ray fluorescence facilities which will be available at the NSLS.

16. ENERGY TRANSFER IN CHEMICAL KINETICS	4.0	01-01
R. E. Weston		

The energy distribution in products of chemical reactions provides a sensitive probe of the reaction mechanism. Collisional energy transfer from excited atoms or molecules perturbs the energy distribution and plays an important role in the reaction mechanism. In this program the transfer of both electronic and vibrational energy is being studied. In both cases atoms or molecules are produced in specific excited states by a pulse of ultraviolet, visible, or infrared radiation. The excited species can transfer energy to another molecule by collision, or can spontaneously lose energy by emission of radiation. The competition between these two processes leads to a decrease in observed fluorescence lifetime, which can be related to a cross section for energy transfer. In addition, laser-induced reactions--unimolecular reactions, bimolecular reactions, and photo-dissociation of vibrationally excited molecules--are being investigated. The laser energy absorption process, energy flow within excited molecules, and energy transfer from excited species are studied.

Chemistry Department, BNL, continued

17. CHEMISTRY OF ENERGETIC ATOMS: BASIC 4.7 01-01
RESEARCH AND APPLICATIONS
A. P. Wolf, R. M. Lambrecht

This program is devoted to the study of the chemistry of atomic and molecular species which are either in energy-rich states or are of exceptionally high chemical reactivity. These may be neutral or charged reactants in ground or electronically excited states, reactants with high kinetic energies, or species which react with high efficiency. Included are reactive intermediates produced by nuclear processes, reactions of C, N, O, and halogen atoms, and studies of atom-atom and atom-molecule reactions in an energy range inaccessible by conventional methods. Atomic species are also produced in known electronic states and with a known temperature by use of a microwave discharge. New methods of generation will include the use of synchrotron "light" to produce high concentrations of molecular ions in reactive media and the development of a new type of ion accelerator to produce intense beams of singly-charged atoms and low molecular weight species. Spectroscopic and chemical techniques are used to identify reactants and products and to determine rates of gas phase reactions.

Photochemical and Radiation Sciences

Department of Energy and Environment
 Brookhaven National Laboratory
 Upton, New York 11973

Total \$910,000

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|-------------------------------------|-----|-------|
| 18. PORPHYRIN CHEMISTRY
J. Fajer | 6.7 | 01-01 |
|-------------------------------------|-----|-------|

This program addresses 1) the role of porphyrin derivatives in the photosynthetic conversion of light into chemical energy, 2) the catalytic function of porphyrins in bioenergetic reactions, and 3) applications of these reactions to biomimetic solar energy transduction and to photocatalysis for the fixation of carbon and nitrogen. The work encompasses synthetic, structural, physical and theoretical chemistry, and presently includes the identification of the primary electron acceptors in photosystems I and II of green plants; electron-electron double resonance to estimate distances between acceptors; theoretical modelling of ligand effects, substituent orientation and hydrogen bonding induced by neighboring molecules on the properties of chlorophyll radicals; x-ray studies of structural and stereochemical changes in porphyrins caused by the gain or loss of electrons; synthetic models of porphyrin-mediated biocatalytic generation of ammonia (isobacteriochlorins); and picosecond electron transfer in cofacial diporphyrin analogs of the molecular arrays currently believed to effect the primary photoacts in photosynthesis.

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| 19. INVESTIGATION OF CHEMICAL PROPERTIES
AND REACTIONS OF MONO- AND DINUCLEAR
FERROCENE DERIVATIVES
M. Hillman | 2.4 | 01-01 |
|---|-----|-------|

This program is an investigation of the preparation and properties of unusual metallocenes and related compounds that are expected to have application in the energy program, especially towards the splitting of water. Particularly, for the oxidation of water a bridged ferrocene derivative is being prepared that can be attached to a silicon electrode. The oxidized state of the compound has a potential high enough to oxidize water and is stable under the conditions required. For the reduction of water, a bridged bisfulvalenedi-iron derivative is being prepared. This compound has tilted Cp rings and is expected to be protonated more easily than the parent non-bridged derivative and therefore to release hydrogen at a lower pH.

Department of Energy and Environment, BNL, continued

20. KINETICS AND MECHANISMS OF CHEMICAL PROCESSES RELATED TO THE DEVELOPMENT AND USE OF ENERGY
J. W. Sutherland 3.1 01-01

This research is directed toward understanding: (a) the modifying influence of surface environment on the basic photophysical and photochemical properties of selected molecules adsorbed on high surface area solids; and, (b) the photochemistry of hydrazine. The investigation into the photochemistry of pyrene adsorbed on porous glass continues; short-lived absorbing species, prompt and delayed fluorescence properties and absorption and excitation spectra are being studied as functions of surface coverage, light intensity and the presence of known electron scavengers and excited state quenchers. Preliminary studies with hydrocarbon sorbates having different physical properties (e.g., ionization potential, electron affinity and acid strength) have begun. The photolysis of solutions of hydrazine in acetonitrile is being investigated. The effects of concentration, temperature and flash intensity on the yields and on the kinetics of the transient species formed on flash photolysis are being examined. These data, together with analyses of the permanent products formed, are being used to describe mechanisms for the photoreactions of hydrazine.

Photochemical and Radiation Sciences

Chemical Biodynamics Division
 Lawrence Berkeley Laboratory
 University of California
 Berkeley, California 94720

21. ARTIFICIAL PHOTOSYNTHESIS 4.5 01-01
 M. Calvin, J. W. Otvos

This research is directed toward devising synthetic systems to accomplish the transfer of photoelectrons across phase boundaries, the way natural chloroplasts convert quanta into chemical energy. One system consists of lipid vesicles with EDTA inside, surfactant ruthenium complex in the bilayer wall, and methylviologen outside. Ionophores to facilitate ion movement through the membrane (e.g., valinomycin) give the control of the electric field across the membrane. Twelve-fold enhancements in quantum yield have been obtained. Water-in-oil microemulsions are also under study. Still another system is provided by 40 Å diameter colloidal SiO₂ particles. With zinc tetrapyrrolyl porphyrin as a multiply charged photosensitizer, neutral propylviologen sulfonate as electron acceptor, and triethanolamine as donor, quantum yield can be studied as a function of factors that change the surface charge: pH and ionic strength. Ten-fold increases in quantum yield due to the SiO₂ particles have been demonstrated. Flow dialysis and flash photolysis experiments are in progress to determine colloid binding properties and reaction kinetics.

22. PHOTON CONVERSION 2.0 01-01
 G. C. Pimentel, J. Clark

This research is directed toward the study of the chemistry of electronically excited molecules and the design of systems that facilitate chemical storage of photon energy. On the picosecond time scale, proton transfer kinetics for the intramolecular H-bond of electronically excited 1-naphthol-2-sulfonate have been measured. This work will be extended to appropriately substituted naphthols. Other picosecond studies are beginning on excited state electron transfer between aromatic hydrocarbons and amines in solvents of different polarity. Apparatus is being assembled for dye laser excitation of endothermic chemical reactions in cryogenic solids. Reaction paths and competing processes will be followed through in situ infrared identification of products, measurements of quantum yields, and chemiluminescence of electronically excited products. Mercury-photosensitized reactions furnish good test systems since mercury atoms can be selectively excited either to singlet or triplet states, which display different excimer chemistry. Construction of apparatus for 10 nanosecond infrared spectroscopy has begun.

Photochemical and Radiation Sciences

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total \$370,000

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|---|-----|-------|
| 23. PHOTOCHEMISTRY OF MATERIALS IN THE STRATOSPHERE
H. S. Johnston | 3.8 | 01-01 |
|---|-----|-------|

With primary emphasis on stratospheric ozone, this project studies atmospheric photochemistry through laboratory measurements, by interpretation of atmospheric observations made by others, and with theoretical models. Photochemical reactions are initiated by laser flash photolysis; the concentrations of atomic or free-radical species, such as Cl, O, HO, and NO are followed by resonance fluorescence; and the concentration of the nitrate free radical NO_3 is followed by laser absorption. Rate constants are determined for reactions of Cl with ClNO, ClNO₂, and HNO₃, and the product yield of NO_3 is found for reactions such as HO + HNO₃. An improved method is being developed for the production of peroxy-nitric acid, and its photochemical reactions are being studied. As atmospheric scientists report measurements of stratospheric species, such as N₂O, HCl, CH₄, H₂O, NO₂, Cl, HOO, and O, these results are interpreted in terms of their contribution to the instantaneous global ozone balance.

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| 24. PHOTON-ASSISTED SURFACE REACTIONS, MATERIALS AND MECHANISMS
G. A. Somorjai | 1.0 | 01-01 |
|---|-----|-------|

The photon-assisted dissociation of water vapor and gaseous carbon dioxide, and subsequent catalyzed surface reactions of these molecules are studied. Transition metal oxide (SrTiO₃, Fe₃O₄) surfaces are utilized to obtain H₂, CO, CH₄, O₂, and other small molecules by photochemical means. The reactions are carried out on well characterized crystal surfaces. The surface reaction mechanisms and the nature of the surface reaction intermediates are studied by electron spectroscopies (XPS, UPS, HREELS) and the reaction is monitored by gas chromatography and mass spectroscopy.

Photochemical and Radiation Sciences

Notre Dame Radiation Laboratory
 University of Notre Dame
 Notre Dame, Indiana 46556

Total \$2,232,000

25. THEORETICAL STUDIES ON REACTING SYSTEMS 5.3 01-01
 D. M. Chipman, W. M. Huo, J. J. Kozak

Quantum and statistical mechanics methods are being developed to interpret phenomena in radiation chemistry and photochemistry, especially those involved in chemical-dynamic processes related to energy storage and transfer. New quantum mechanical approaches are being used to provide information on electronic and molecular structure, potential energy surfaces, reaction mechanisms, electron-solvent interactions and spin density distributions in free radicals. Quantum dynamical aspects of the interaction of radiation with matter, and specifically the temporal decay of excited states of two- and three-level atomic and molecular systems, are being studied using new analytical techniques developed in this laboratory for solving the time-dependent Schrodinger equation. A comprehensive theory of photo- and radiation-induced redox reactions in organized molecular assemblies is being developed. These latter studies have considerable relevance to our understanding of experiments in which organizes may be applied in photochemical processes to effect the storage of solar energy.

26. ORGANIC PHOTOCHEMICAL PROCESSES 4.8 01-01
 P. K. Das, M. V. George, T. Kilp

Photochemical processes in organic systems are being examined to provide information on the role of intermediates including radicals, biradicals and triplet states, on energy transfer mechanisms and on the resultant overall photochemistry. Currently emphasis is on the use of laser flash photolysis techniques to study both intermolecular and intramolecular energy migration. Studies include examination of intermolecular energy transfer between quasi-isoenergetic triplets, intramolecular transfer in molecules containing two chromophores, energy hopping along a polymeric chain, and energy trapping in copolymers containing several types of chromophores. These studies on energy migration in polymers are particularly relevant to photosynthesis and to possibilities for enhancing the properties of polymers toward photodegradation or photostabilization. Other studies in progress are directed toward understanding photochemical processes involving bi-radicals, particularly those produced from aromatic ketones and toward the reactions of photolytically produced oxygen centered radicals.

Notre Dame Radiation Laboratory, continued

27. INORGANIC PHOTOCHEMICAL STUDIES 4.5 01-01
G. J. Ferraudi

The photochemical properties of transition metal ion complexes with macrocyclic ligands are being investigated. The nature of the metal center, the effect of ligand structure, and the overlap of the π system with the electronic density of the metal ion are being examined using different members of a given family of macrocycles. The dependence variations of the photochemical response on the electronic configuration of the complex are being investigated to evaluate the importance of different contributions in various regions of the spectrum. Reference pulse radiolytic experiments are also being carried out to provide spectroscopic and reaction rate information on redox intermediates. Many macrocyclic complexes of metal ions undergo photochemically produced electron transfer with light in the visible region of the spectrum and so have potential applications for initiating processes with solar radiation. Copper complexes are being particularly examined since they absorb visible light and photosensitization by the metal center has been shown to result in chemical changes in the macrocyclic ligand.

28. MICROWAVE STUDIES ON RADIATION 3.2 01-01
CHEMICALLY PRODUCED INTERMEDIATES
R. W. Fessenden

Time-resolved ESR experiments are being carried out to provide information on the reaction kinetics of specific radicals and on spin population dynamics of radiation produced radicals. Both pulsed microwave and pulse radiolysis methods are used. The latter provide quantitative data for tests of the current theories of chemically induced dynamic electron polarization (CIDEP). More conventional steady-state ESR experiments are used to study electron distributions in radicals, radical formation mechanisms and to examine electron exchange and protonation equilibria. These latter experiments form part of an integrated approach using a number of techniques to give detailed data on the mechanisms of radiation chemical reactions. Microwave conductivity is also being used to study electron attachment processes in gases at pressures of one atmosphere and above in order to determine the importance of Van der Waal's complexes in these reactions and to examine ionization phenomena in dielectric liquids.

Notre Dame Radiation Laboratory, continued

29. TIME RESOLVED STUDIES OF PHOTOLYTIC REACTIONS 3.2 01-01
R. W. Fessenden

Time resolved microwave absorption methods are applied to characterize the charge distribution in intermediates produced by laser excitation. Particular attention is being given to measuring the degree of charge separation in various radicals, excited states (triplets) and exciplexes. Parallel optical absorption experiments are being carried out to provide more complete descriptions of the photolytic processes involved. Optical absorption methods are also being used to examine direct oxidation by photoionization for comparison with the intermediates produced by secondary oxidation with OH and SO₄. Double pulse experiments are used to characterize the absorption bands of intermediates and to better understand their energy levels. These investigations are complimented by steady state and time resolved ESR studies of photolytically produced radicals.

30. THEORETICAL ASPECTS OF RADIATION CHEMISTRY 3.0 01-01
K. Funabashi, W. H. Hamill,
A. Mozumder

Attention is being focused on cross sections for capture of thermal electrons, problems associated with electron thermalization especially with respect to determinations of thermalization times and distances, dielectric relaxation in polar liquids, influence of field dependent transport coefficients on escape probabilities, examination of the random-walk model for electron scavenging, theoretical studies of the optical absorption of solvated and trapped electrons, studies of the mechanisms for localization of energy in irradiated polyatomic systems and on the nature and properties of reactions at early times particularly as they apply to track effects. Contributions of secondary electrons in the reactions within heavy particle tracks are being examined. Conclusions from these studies are important both to radiation chemistry and to other areas where ions are important such as reactions of ions in the atmosphere and electrical properties of insulators.

Notre Dame Radiation Laboratory, continued

31. SPECTROSCOPY OF REACTION INTERMEDIATES 3.9 01-01
 J. Hardwick, J. J. Bentley, Jr.,
 Y. Inel, G.N.R. Tripathi, D. Winicur

Spectroscopic studies of reactive species produced in radiolysis, photolysis and combustion processes are being carried out to identify those species, determine their molecular structures, probe their excited vibrational and electronic states, determine the inter- and intramolecular pathways through which excess energy is redistributed and to examine their reaction kinetics. High resolution absorption and emission spectroscopic methods together with laser excited fluorescence are used to determine rotational, vibrational and electronic energies of radicals and other intermediates present in flames. Gas phase kinetic processes involving combustion intermediates such as $\text{CH}_3\text{O}\cdot$ are followed spectroscopically. Radicals are also being studied in both the liquid and solid phase by resonance Raman techniques. Photoacoustic techniques are used to examine the collision-induced absorption of forbidden vibrational modes to provide information on the transient dipole moments and molecular distortions which result from molecular collisions.

32. ELECTRON TRANSFER REACTIONS 6.0 01-01
 P. Neta, H. Levanon

Pulse radiolysis techniques are being used to characterize the kinetic properties of short lived transient species involved in electron transfer or redox mechanisms. Approaches developed in this laboratory provide methods for examining electron transfer equilibria and allow the determination of one-electron oxidation or reduction potentials for various types of organic radicals. Details of the oxidation and reduction of organic molecules by both organic and inorganic radicals are being examined. Additionally, time resolved studies are used to determine the reactivities of the intermediates following radiation initiated cleavage of both organic compounds and inorganic ions. Special attention is given to electron transfer reactions involving porphyrins and similarly large molecules and also to intramolecular electron transfer within organic radicals and metal complexes. The ultimate aim of these various studies is to expand our understanding of reaction intermediates so as to be able to predict their role in both radiation and conventional chemical systems.

Notre Dame Radiation Laboratory, continued

33. INFLUENCE OF ORDERED MOLECULAR ASSEMBLIES ON CHEMICAL PROCESSES 3.8 01-01
L. K. Patterson

Basic information governing relationships between the organization of hydrophobically structured surfactant assemblies and the influence these assemblies have on the kinetics of bulk phase, interfacial and surface processes is being developed. Unique properties include non-homogenous distribution of reactants, surface orientation and surface charge effects, changes in chemistry resulting from reduction in dimensionality of the reactant phase, and compartmentalization of the reaction into microregions with well defined boundaries. The possibility for kinetic control over photochemical processes has significant implications in the design of systems appropriate to the chemical storage of energy. Work is being increasingly focussed on behavior in spread monolayers where greater control may be exerted over the character of the assembly and where very little attention has previously been paid because of experimental limitations. Techniques applied in these studies include chemical measurements, time resolved absorption spectroscopy and both steady state and time-resolved fluorescence spectroscopy.

34. RADIATION CHEMISTRY DATA CENTER 1.0 01-01
A. B. Ross, W. P. Helman, G. Hug,
I. Carmichael

The Radiation Chemistry Data Center (RCDC) carries out a continuous survey of the literature of radiation chemistry and photochemistry, critically examines and compiles experimental data on intermediates produced by light and ionizing radiation and provides to the scientific community a variety of information services from its data bank. The Biweekly List of Papers on Radiation Chemistry and Photochemistry is issued regularly to interested subscribers. Critically reviewed and evaluated data on reaction intermediates prepared by the Center are of general importance to proper considerations of both the basic scientific and technological application of chemical processes, particularly those involved in radiation chemical and photochemical (solar energy) programs.

Notre Dame Radiation Laboratory, continued

35. RADIATION INDUCED REACTIONS 6.8 01-01
R. H. Schuler, E. Janata,
L. K. Patterson, G.N.R. Tripathi

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 both intermediates in time resolved studies and for analysis of ultimate products. Attention is, to a large extent, focussed on competition between recombination processes that occur within the radiation produced track and scavenging by added solutes. Interpretation of the data is enhanced by improvements in dosimetry and time resolution at the LINAC facility which allow optical and conductometric pulse radiolytic studies to be carried out at nsec times. Studies are also being carried out at the Notre Dame Heavy Ion Facility to examine track effects in radiation chemical reactions induced by low Z ions having LET's of 1-100 ev/Angstrom. These track studies are complemented by studies at very high intensities using a Febetron as a radiation source.

36. ENERGY TRANSFER IN ATOMIC AND MOLECULAR SYSTEMS 2.0 01-01
D. H. Winicur

Molecular beam methods are being used to examine the mechanisms, cross sections and intermediate species involved in energy transfer in elementary processes. Interactions between metastable, excited rare-gas atom and various small molecules such CO₂, H₂O, (CH₃)₂O, H₂, and F₂ are determined from measurements of differential scattering cross sections using crossed-molecular beams. The results from these experiments provide detailed information on the nature of the interactions during the molecular collision, indicate the states present immediately after the initial energy transfer and allow a determination of the potential-energy curves for the interacting species and of translational-to-rotational and translational-to-vibrational energy exchange. Understanding of energy transfer mechanisms is of particular importance to the development of chemical lasers and it is planned to extend these studies to a wide variety of energy transformations of interest to radiation, photo-, laser and atmospheric chemistry.

Photochemical and Radiation Sciences

Research Division
 Solar Energy Research Institute
 1617 Cole Boulevard
 Golden, Colorado 80401

Total \$320,000

37. PHOTOPHYSICS AND PHOTOCHEMISTRY OF CHLOROPHYLLS, PORPHYRINS AND MODEL SYSTEMS FOR ARTIFICIAL PHOTOSYNTHESIS
 J. S. Connolly 1.0 01-01

This research addresses the area of sensitized solar photochemistry in its broadest sense. Thus it is concerned with spectroscopic and photophysical studies of energy transfer as well as reversible and irreversible electron-transfer reactions of excited states in a variety of organic and organometallic systems. The experimental focus is on the properties of natural photosensitizers (chlorophylls, porphyrins) with additional emphasis on model systems for artificial photosynthesis. The goal is to contribute to an improved understanding of the fundamental molecular properties required for efficient light-induced electron transfer in photosynthesis and photocatalysis, broadly defined. A systematic study has been initiated on the influences of molecular environment and structure on the excited-state properties of chlorophylls, pheophytins and some other porphyrin-related molecules. In the model systems area, laser flash photolysis experiments are being carried out on covalently linked donor-acceptor complexes to study the kinetics and mechanisms of light-induced electron transfer.

38. BASIC PHOTOELECTROCHEMISTRY RESEARCH
 A. J. Nozik, J. A. Turner, A. J. Frank 2.5 01-01

Research is being conducted on new mechanisms of photoinduced charge transfer across semiconductor-electrolyte interfaces and on the behavior of semiconductor photoelectrodes that are modified with surface layers of conducting organic polymers. Hot carrier effects, involving the injection of photogenerated charge carriers into the electrolyte before they fully thermalize in the semiconductor, are being studied both theoretically and experimentally. The theoretical work involves calculations of the kinetics of hot carrier injection and the thermodynamical consequences for maximum conversion efficiency. Experimental work involves probing for hot carrier injection by looking for chemical effects that could only arise from hot carriers, such as supra-band-edge reactions and collision excitation of luminescent molecules. Organic conducting polymers on semiconductor electrodes are being studied with respect to their influence on charge transfer kinetics and the related photo-stability properties of the semiconductor electrode.

Chemical Physics

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total \$623,000

39. STATISTICAL MECHANICS OF GASEOUS SYSTEMS 2.0 01-02
D. K. Hoffman

This work has two basic aspects. One is the development of mathematical models which predict the spatial correlation of events which occur sequentially and irreversibly at sites on a lattice. In practical application the "lattice" is the regular array of (bulk or surface) sites of a solid at which "events" such as irreversible adsorption of atomic or molecular species, corrosion, radiation damage, or structural transformations can occur. The aim is to show how the energetic or geometric features of the system determine the spatial distributions of such events. These distributions in turn affect bulk properties of the system. A second aspect of the work is to understand transport and relaxation processes in polyatomic gases. In some cases, e.g., those involving gas phase energy transfer, the processes themselves are important. In other cases they provide a macroscopic probe of the collision dynamics. Current emphasis concerns collision models and approximation schemes from which transport and relaxation cross sections which sensitively depend on inelastic collisions can be calculated with accuracy.

40. ATOMIC MOLECULAR AND FREE RADICALS 2.0 01-02
CROSSED BEAM KINETICS
C. Y. Ng

This program emphasizes obtaining accurate thermochemical data needed to characterize elementary chemical reactions related to combustion. By combining the molecular beam method and photoionization mass spectrometry, novel experimental approaches are being developed, which make it possible to isolate and study pertinent reactants and products. Ongoing projects include high resolution photoionization studies of simple molecules such as SO₂, H₂S, NO₂, C₂H₂, C₂H₄, and C₃H₆. The high Rydberg state and ion-molecule reactions of these molecules are being investigated by photoionization of the neutral van der Waals dimers and clusters of these molecules formed in a supersonic jet.

Ames Laboratory, continued

41. MOLECULAR BONDING THEORY 3.0 01-02
 K. Ruedenberg, S. T. Elbert

This project concerns determinations of molecular properties and of energy changes during chemical reactions through quantum chemical calculations of electronic structures. Its aim is prediction of reaction and activation energies for elusive intermediates and transition states which are needed in energy-related research but difficult or impossible to obtain experimentally. It includes studies of oxidation-reduction and exchange reactions involving carbon, nitrogen, oxygen and hydrogen to elucidate reactions occurring during combustion, in the atmosphere, and during hydrogenations. The method of Full Optimized Reaction Space (FORS) for an unrestricted description of electronic rearrangements along chemical reaction paths has been developed. The FORS model predicts reactive energy changes and their implications for reaction mechanisms within chemical accuracy. Analysis of the FORS model is underway to develop quantitative interpretative concepts which aid intuitive reasoning, consistent with ab-initio calculations, so as to anticipate the consequences of reactive changes with minimal computation.

42. ION CHEMISTRY - MASS SPECTROSCOPY 2.0 01-02
 H. J. Svec, G. D. Flesch

This program emphasizes studies of the production of gaseous ions and neutral products resulting when molecules interact with energetic electrons. The development of a double ended, dual ionization chamber mass spectrometer facilitates this work. Studies of the tetramethyl derivatives of Si, Ge, Sn, and Pb and N₂, O₂ and mixtures thereof have elucidated excited states of the neutral species far above their ionization energies. These excited states have lifetimes $\gtrsim 10^{-6}$ s. Autoionization, autoionization/dissociation, molecule/molecule interactions, and dissociation to neutral products have been observed. A new ion and excited state chemistry, unavailable via optical spectroscopy is now tractable. For example, the onset energy needed to produce NO as a result of interactions between excited N₂ and O₂ has been determined. Studies of mixtures of O₂ and hydrocarbons have implications in combustion processes.

Chemical Physics

Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Total \$1,290,000

43. HIGH-RESOLUTION SPECTROSCOPY 3.0 01-02
H. M. Crosswhite, F. S. Tomkins,
K. T. Lu

Optical spectroscopy is being used to examine the fundamental electronic properties of matter at the atomic level, using large grating spectrographs augmented by N₂- and YAG-driven tunable dye lasers and large superconducting magnets, for studies ranging from diamagnetic behavior of atomic energy levels to the nature of photoionizing resonances, and to dynamic phenomena such as transition rates and collisional line-broadening. Four-wave mixing phenomena in nonlinear optical media such as Mg, Be, Hg and Zn vapors are used for the generation of tunable coherent vacuum ultraviolet radiation for use in extending the studies to higher energies in the photoionizing region and for studies of nonlinear phenomena in their own right. Mercury vapor appears to be particularly useful as a nonlinear medium because of the low operating temperatures required and its high efficiency. An important part of this program is devoted to developing the tunable coherent vacuum ultraviolet radiation for high-resolution investigations of high-energy-level phenomena in atomic and molecular vapors and plasmas.

44. THEORETICAL CHEMISTRY 4.3 01-02
T. H. Dunning, Jr., G. P. Das,
L. B. Harding, A. F. Wagner

The theoretical chemistry program emphasizes studies of reactions of importance in combustion as well as studies of the chemistry of metal atom clusters. The combustion chemistry activity is focused on the theoretical characterization of the chemical reactions of small free radical species, with an emphasis on reactions of importance in the oxidation of hydrogen and simple hydrocarbon fuels (methane, acetylene, ethylene and formaldehyde). The objectives are to develop a qualitative understanding of these reactions in order to predict mechanisms and approximate rate constants and to develop quantitative methods that allow computation of detailed rate constants. Metal cluster chemistry research is focused on the theoretical characterization of the structure, properties and reactions of clusters of metal atoms, in particular of species relevant to a fundamental understanding of catalysis.

Chemistry Division, ANL, continued

45. CHEMISTRY OF THE MHD PROCESS 0.4 01-02
J. C. Hindman

The objectives of the project are (1) to determine what chemical processes are involved in controlling the conductivity of a seeded (K) coal-fired open-cycle MHD generator, (2) to determine whether or not kinetic processes are important, and (3) to devise methods for maximizing the ionization (conductivity) of the plasma. Laser spectroscopic methods are being used as non-intrusive probes for these studies.

46. MOLECULAR BEAM AND METAL CLUSTER 4.4 01-02
CHEMISTRY RESEARCH
S. Wexler, E. K. Parks,
T. H. Dunning, Jr.

In a program designed to study the mechanisms and dynamics of heterogeneous catalysis on the molecular level, beams of catalytically active naked metal atom clusters are generated and their physical and chemical properties are characterized by in-flight molecular beam techniques. Beams of Ni, Ag, Cu, Al and Fe clusters with 2 to \sim 20 atoms are or will be produced by a novel high temperature source and gas flow quench system. Electronic and spectral properties are determined by pulsed-laser multiphoton ionization spectroscopy, laser-induced fluorescence, collisional ionization and matrix isolation spectroscopy. The experimental results are correlated with ab initio theoretical calculations. In a second program, investigation, by a crossed-molecular beam method, of ion-pair formation from dissociation of molecules by collision with hyperthermal atoms and molecules is being continued. From these studies are derived the factors which are important in the transfer of translational energy to internal energy. This transfer regulates the breakage and formation of chemical bonds in bimolecular collisions.

Chemical Physics

Chemistry Department
 Brookhaven National Laboratory
 Upton, New York 11973

Total \$2,880,000

47. NEUTRON SCATTERING AND MOLECULAR
 STRUCTURE AND DYNAMICS 5.5 01-02
 L. M. Corliss, J. M. Hastings,
 T. F. Koetzle, A. Kvik,
 R. K. McMullan, R. Thomas

X-ray and neutron scattering methods are used to solve significant problems in molecular structure, magnetism, phase transformations, and the dynamical properties of solids. The structural program emphasizes structures where hydrogen atoms are important, structures containing magnetic ions, and disordered or partially-ordered structures, since in these areas neutron diffraction, alone, or in combination with x-ray diffraction, has unique advantages. Systems studied include organometallic substances, transition-metal hydrides and hydride coordination compounds, ionic conductors, ferroelectrics, magnetic crystals, and organic crystals. Studies combining x-ray and neutron diffraction are also undertaken to examine molecular charge-density distributions. Inelastic neutron scattering is used to study atomic motion in solids. In magnetic systems one can obtain the spatial distribution of magnetization and the behavior of spontaneous fluctuations, both essential to understanding magnetic phase diagrams, their associated first- and second-order transitions, and multicritical points.

48. THEORETICAL CHEMISTRY 4.5 01-02
 S. Ehrenson, J. T. Muckerman,
 M. D. Newton

The goals of this program are to apply theoretical methods to the study of energy flow in chemical reactions and to the elucidation of molecular interactions involved in the storage and interconversion of energy including phenomena associated with charged species (i.e., solvation and charge-transfer processes). The methods principally used are ab initio and semiempirical calculations of the energies and structures of molecules in specific electronic states, and classical and semiclassical treatments of the nuclear motion in kinetic processes involving these systems. Specific chemical problems of interest are: ab initio models for aqueous charge-transfer processes, hydrogen bonding in hydroxylic systems; the electronic structure of transition metal clusters and their chemisorptive interaction with organic molecules; the nature of chemical bonding in silicates, dielectric effects of solvents surrounding cavities of various shapes; dynamics and energetics of elementary combustion reactions; and dynamics of reactions involving excited states of atoms and molecules.

Chemistry Department, BNL, continued

49. ION-MOLECULE REACTIONS 5.5 01-02
L. Friedman, R. Beuhler

High molecular weight mass spectrometric techniques are used to investigate nucleation processes responsible for the formation of cluster ions and neutral microclusters. Immediate goals are the development of cluster-ion sources and their exploitation as a basic research tool. Present capability of mass analysis of molecular species with m/e values up to approximately 200,000 is being expanded to higher m/e values using high voltage ion post acceleration and of time of flight mass analytical techniques. Ion source facilities capable of generation of plasmas from gases cooled to temperatures as low as 10 K will be used to study cluster ion generation from inert gases and diatomic molecular species. The generation of cluster ions from hydrogen isotopes is considered a major task objective because of the potential role these cluster-ions may have in the study of controlled thermonuclear reactions. Energy transfer processes of cluster ions in gas phase collision processes and on impact with solid surfaces will be investigated.

50. MOLECULAR BEAM STUDIES OF CHEMICAL 1.6 01-02
DYNAMICS USING SHORT-LIVED RADIO-
ACTIVITY AND SYNCHROTRON LIGHT
J. R. Grover and M. White

A user-oriented windowless experimental facility for gas phase studies is being designed and built for interfacing with the NSLS. The planned BNL use of this facility features a nozzle molecular beam apparatus in which strongly cooled molecules, radicals, and clusters are studied by mass spectrometry and electron spectrometry, utilizing the tunable vacuum ultraviolet radiation for photo-ionization. Long-term prospects include a unique crossed beam capability for measuring angle-differential cross sections, plus detailed energy disposal patterns, for elementary reactions involving four or more atoms and multiple reaction pathways. In addition a crossed molecular beam technique having one of the reagent beams labeled with a short-lived ($< 10^{-1}$ sec) radioactive isotope is being used to measure absolute differential cross sections for reactive scattering. The basic goal of this work is to provide definitive experimental determinations of reactive potential hypersurfaces, to test and calibrate semiempirical theories now under development.

Chemistry Department, BNL, continued

51. HIGH FLUX BEAM REACTOR OPERATIONS
G. C. Kinne

01-02

Several research programs at Brookhaven are centered at the High Flux Beam Reactor (HFBR), which was specifically designed for neutron beam research. It provides thermal neutron beams which are as free as possible of contamination by γ rays and high energy neutrons. There are a total of nine ports (numbered H-1 through H-9) from which neutron beams can be extracted. In addition, there are seven vertical thimbles (numbered V-10 through V-16) which provide a variety of neutron energy spectra for sample irradiations. At its original power level of 40 megawatts, the HFBR provides a total flux of 1.6×10^{15} neutrons/cm²-sec (peak thermal flux 7×10^{14} neutrons/cm²-sec). A construction project to raise the power level to 60 megawatts has been completed, and as soon as DOE safety review is completed and operating approval received, the power level will be increased to 60 megawatts. This will result in a 50% increase in these fluxes, making the HFBR at least equal to the best in the world in these categories.

Chemical Physics

Department of Energy and Environment
 Brookhaven National Laboratory
 Upton, New York 11973

Total \$470,000

52. ELECTROCHEMISTRY 2.6 01-02
 S. Feldberg

Research in this program has been carried out in three major areas. 1. Studies of electron transport and ion transport across bilayer lipid membranes (blm): Metallochlorins have been found to facilitate electron transport across blm. Mg-etiochlorin (MgC) is particularly effective when coupled with ferri-/ferrocyanide in the aqueous phases. About 75% of the charge transport is due to electron transport. Preliminary studies using Zn-octaethylchlorin (ZnC) indicate that it is a less effective electron transporting agent than MgC and simultaneously transports hydroxide ion. 2. Studies of the reactions of the excited states of Mg-octaethylporphyrin (P): Experimental analysis of the reactions of the triplet (T) of P characterizes a number of triplet reactions-T to give 2P, excited singlet and delayed fluorescence, or ions P^+ and P^- . 3. Theoretical studies of the effects of light pulses on semiconductor electrodes: A model for the analysis of the relaxation of photopotentials of semiconductor electrodes following pulsed light excitation is being developed to describe a variety of experimental observations. This is a collaborative effort with S. Gottesfeld, University of Israel.

53. KINETICS AND MECHANISMS OF ALTERNATIVE 3.5 01-02
 FUELS COMBUSTION
 R. Bruce Klemm

The objectives of this task are to investigate the detailed chemical kinetic and mechanistic factors involved in gas phase combustion and pollutant formation processes. Emphasis is placed on alternative fuels that comprise a wide range of fuel types, including methyl and ethyl alcohol, hydrocarbon syn-fuels, and hydrogen. The complementary techniques of discharge flow and flash photolysis are used to determine specific rates for combustion related, elementary atom-molecule reactions. Combined, these methods provide a wide temperature span, $\sim 300-1100\text{K}$, over which direct kinetic studies of combustion initiation reactions and oxidation reactions of combustion intermediates are made. High temperature, absolute rate data for these reactions (e.g., O-atom/alkanes and O-atom/ CH_3OH) are important for the further development of kinetic theories as well as for modelling combustion systems. In addition, a photo-ionization mass spectrometer experiment that utilizes the National Synchrotron Light Source is being developed jointly between the Department of Energy and Environment and the Chemistry Department.

Chemical Physics

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total \$80,000

54. UNIMOLECULAR KINETICS
N. Brown

1.3

01-02

Combustion chemistry consists of complex, multi-step chain mechanisms involving reactive radicals which are present in small concentrations. The complexity of the mechanisms, the inherent difficulties of working in high temperature environments, and the large number of species involved with the oxidation of any fuel make the study of combustion chemistry quite difficult. Our current research was initiated in FY 79 is concerned with the application of theoretical chemical kinetics to study high temperature kinetics important in combustion processes. Emphasis has been placed upon characterizing intramolecular energy transfer in molecules. This is important in describing high pressure limit and fall-off regime unimolecular reactions. Rate coefficients of triatomic molecules important in combustion processes are determined using statistical adiabatic theories. Intramolecular energy transfer leading to dissociation is being studied dynamically for the molecule HO_2 utilizing a realistic potential energy surface. In addition, we have initiated a dynamical study of the reaction: $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ which is of major importance in water formation in hydrogen and hydrocarbon oxidation schemes.

Chemical Physics

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total \$1,929,800

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| 55. ENERGY TRANSFER AND STRUCTURAL STUDIES OF
MOLECULES ON SURFACES
C. B. Harris | 4.4 | 01-02 |
|--|-----|-------|

The purpose of this research program is to develop spectroscopic techniques for investigating the electronic and molecular structure of molecules adsorbed on catalytic metal surfaces. Using these techniques, a variety of problems are being studied including (a) investigating the changes induced in the molecular and electronic structure of aromatic hydrocarbons upon physi- and chemisorption to catalytic metal surfaces, (b) the study of ring cracking reactions of aromatic hydrocarbons on nickel surfaces, (c) the study of the vibrational structure of molecules adsorbed on metal surfaces via Laser Raman Scattering, and finally (d) the study of the dynamics of energy transfer from adsorbed molecules to metal surfaces as a function of their interaction with the metal surface as well as distance away from the surface.

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| 56. CROSSED MOLECULAR BEAMS
Y. T. Lee | 6.3 | 01-02 |
|--|-----|-------|

The primary goal of this research is the elucidation of the dynamics of elementary molecular processes and the energetics of highly reactive free radicals, weakly bound complexes, and ions. Mechanistic and dynamical information about chemical reactions is obtained from angular and velocity distributions of products from the single collision reactive event. Oxygen atom reactions with hydrocarbons are being studied to identify primary products and final energy partitioning. Reactive scattering resonances are being sought in collisions of neutral species, $F + H_2$, D_2 , and in ion molecule reactions, $H_2^+ + D_2$. Many experiments are coupling lasers with molecular beams. Laser excitation of the reactant beam is being used to investigate reactions of electronically excited atoms and molecules. The dynamics of photodissociation of polyatomic molecules, including the weakly bound Van der Waals complexes, are being determined in studies of single and multiple photon processes.

Materials and Molecular Research Division, LBL, continued

57. CHEMICAL DYNAMICS STUDIES 1.0 01-02
B. H. Mahan and Y. T. Lee

Derivation of fundamental and practical information about chemical dynamics from the study of collision processes which involve ions, molecules, and photons in the gas phase. Methods of predicting the rates of chemical reactions, energy transfer processes, collisional dissociations, collisional ionizations and charge transfer processes, using as primary information the electronic energy states of the reactants, products, and intermediates. Prediction of the kinetic behavior of complex systems; reactive and nonreactive scattering by hydrogen of a number of ions that appear prominently as contaminants in hydrogen plasmas. Rapid and economical estimation of the energy distributions of the products of some classes of reactions. A unique apparatus designed to obtain the electronic spectra of mass identified gaseous ions by laser induced fluorescence has been constructed and operated successfully.

58. THEORY OF ATOMIC AND MOLECULAR COLLISION PROCESSES 2.1 01-02
W. H. Miller

This research is primarily involved with the development of theoretical methods and models for describing atomic and molecular collision processes. The overall goal is to understand the dynamics of chemical phenomena at a molecular level and may thus be described as "molecular level chemical kinetics." 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. Certain research topics are more amenable to a completely quantum mechanical approach, and these sorts of theoretical techniques are also used.

Materials and Molecular Research Division, LBL, continued

59. SELECTIVE PHOTOCHEMISTRY 2.8 01-02
C. B. Moore

The emphasis of this research has been on the study of high vibrational overtone excitation to understand coupling among modes at high internal energies, and on the exploration of vibrational photochemistry following excitation. High overtone excitation is best described as vibrational excitation of a single stretching oscillator, a local mode. Through the spectra of alkanes and alkenes, guidelines are developed to assign the spectra of more complicated molecules of photochemical interest. Spectra of halomethanes investigate in detail the coupling of the C-H stretching vibrations to the other molecular motions. Measurements of unimolecular photochemistry following selective overtone excitation are in progress in both gas and liquid phases. Time-resolved dye laser absorption spectroscopy is used to measure combustion-related reactions of HCO. Studies of vibrational relaxation of molecules in cryogenic matrices measure the strength of host-guest interactions in order to determine the feasibility of selective reactions at low temperatures.

60. PHYSICAL CHEMISTRY WITH EMPHASIS ON 2.5 01-02
THERMODYNAMIC PROPERTIES
K. S. Pitzer

One important set of objectives includes the development of a quantum chemistry for heavy atoms where relativistic effects are important and the prediction of numerous properties of molecules containing such heavy atoms. The major relativistic effects, which arise for electrons near the nucleus, are incorporated into effective potentials which then reflect these indirect effects on the valence electrons and their capacity to form chemical bonds. Calculations for Tl_2 show major differences between the relativistic results and nonrelativistic estimates. Results are also available for Tl_2^+ , TlH , and other molecules. Another area of research concerns the statistical thermodynamics of ionic systems including aqueous electrolytes over wide ranges of temperature and pressure as well as plasmas. Emphasis is given to conditions of practical application including those for synthetic fuels and for geothermal energy. Equations have been developed which successfully predict the properties of mixed electrolytes (brines). This work is being extended to wider ranges of temperature and pressure.

Materials and Molecular Research Division, LBL, continued

61. POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS 4.9 01-02
H. F. Schaefer

This research program has two goals, related yet distinct. The first goal is the development of new theoretical and/or computational methods for the description of electrons' behavior in molecules. Specifically, the single outstanding problem in the field is the correlation problems, that of formulating models for going beyond the single-particle or Hartree-Fock approximation. The second goal of this research is to apply these theoretical methods to significant problems of broad chemical interest. Currently, two areas of dominant interest are: (a) model theoretical studies of organometallic compounds, chemisorption, metal clusters and catalysis, and (b) the potential energy surfaces which govern gas-phase chemical reactions. Research in the former area is aimed at a truly molecular understanding of catalysis, a subject critical to future energy requirements, but sometimes approached by brute force trial and error methods. In the latter area, the present research tends toward molecules potentially important in the development of high powered laser systems.

62. PHOTOELECTRON SPECTROSCOPY 8.5 01-02
D. A. Shirley

Electron spectroscopy: electronic structure of matter, as determined by photoelectron spectroscopy and related techniques. The electronic structure of gas-phase species, including high-temperature species, as determined by the use of pulsed synchrotron radiation, including absorption, fluorescence, and time-of-flight photoelectron spectroscopy. Photoelectron angular distributions and correlation-state studies. Electronic structure of solids from angle-resolved, variable-energy photoemission. Atomic and electronic structure of surface-adsorbate systems. Photoelectron spectroscopy of Van der Waals' molecules and other exotic species. Exploration and development of new experimental methods based on synchrotron radiation in the energy range 10-4000 eV, such as photoelectron diffraction and surface EXAFS.

Materials and Molecular Research Division, LBL, continued

63. MOLECULAR BEAM SPECTROSCOPY

3.0

01-02

J. S. Winn

This research program derives fundamental spectroscopic information on molecular states of importance to several practical techniques. A molecular beam electric resonance spectrometer is being used to generate HF and DF in high vibrational states and to measure the dipole moment and other spectroscopic constants in these states. Similar data on other molecules and radicals of importance to combustion processes will be sought. Various visible and UV spectroscopies are being used to study metal carbonyl dissociation mechanisms, thin film formation from such dissociations, and the chemical reactivity of such films. The dissociation of $\text{Fe}(\text{CO})_5$ to $\text{Fe} + 5\text{CO}$ has been characterized under VUV photolysis, electron bombardment, metastable rare gas collisional dissociation, and multiphoton photolysis conditions.

Chemical Physics

National Resource for Computation in Chemistry
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

64. NATIONAL RESOURCE FOR COMPUTATION IN CHEMISTRY 8.0 01-02
W. A. Lester, Jr.

The principal goal of the NRCC is to advance the utilization of computer hardware and software in the chemical sciences. Programs of research, software development, service and education are established in several chemical subdisciplines, including chemical kinetics, crystallography, macromolecular science, physical organic chemistry, quantum chemistry, and statistical mechanics. The focus of effort is: 1) to foster new directions in chemical computation through in-house research and workshops on timely topics; 2) provide generally useable computer programs through the software library and distribution system; 3) encourage efforts at software standardization and portability through workshops, publications and cooperative code development projects; and 4) provide information on new developments in computational hardware and software through benchmarking projects, symposia and NRCC publications.

Chemical Physics

Chemistry Division
 Oak Ridge National Laboratory
 P. O. Box X
 Oak Ridge, Tennessee 37830

Total \$820,000

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| 65. | MOLECULAR RESEARCH WITH ELECTRON
SPECTROSCOPY
T. A. Carlson, M. O. Krause | 2.0 | 01-02 |
|-----|---|-----|-------|

The basic process of ionization and the attendant information on the electronic structure of molecules and atoms is under investigation by means of angle-resolved photoelectron spectroscopy (ARPES). These studies are carried out as a function of photon energy by use of synchrotron radiation. Results are obtained on partial cross sections, angular parameters, auto-ionization, shape resonances and electron correlation. Theoretical calculations are underway to allow the experimental data to be a test of the fundamental understanding of the photoionization process, and to provide the best and most comprehensive basis for evaluating molecular orbital theory. In addition to the ARPES of valence orbitals, experiments on core shells near their ionization thresholds are underway that hold promise for an exciting method for studying chemical bonding.

- | | | | |
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| 66. | THEORETICAL CHEMISTRY
O. H. Crawford | 1.0 | 01-02 |
|-----|---|-----|-------|

This program contributes to a fundamental understanding of atomic and molecular dynamics through the development of appropriate quantum and classical theories. The interaction of high-energy ions with crystalline solids is being studied in connection with accelerator-based experiments at ORNL. The high-velocity limiting form of the stopping power has been derived. Our result supersedes the Bethe-Bloch formula, which is shown to be incorrect for anisotropic media (e.g., graphite). A method for predicting channeled stopping power has been found that agrees closely with experiment. These values are needed for the extraction of depth profiles of crystal dopants from ion scattering data. In another area, a theoretical investigation of surface-enhanced Raman scattering is under way, and experiments are being designed to test this theory and to explore the potential usefulness of this effect for the detection and characterization of species adsorbed at liquid-solid and gas-solid interfaces.

Chemistry Division, ORNL, continued

67. ATOMIC AND MOLECULAR COLLISION DYNAMICS 3.0 01-02
S. Datz, B. K. Annis, H. F. Krause

Basic mechanisms and consequences of atomic and molecular collisions in the gas phase and condensed media are being studied over a broad range in energy. In the thermal and epithermal regions, molecular beam methods are used to study chemical reactions, electron detachment from negative ions, and intermolecular energy transfer. Interest here centers on reactions involved in combustion. At higher (MeV) energies using particle accelerators, correlated collisions in single crystals lead to channeling phenomena. Coherent effects such as resonant excitation permit measurement of crystal fields and provide a form of spectroscopy to study the detailed states of swift ions as they penetrate matter. Coherence in the motion of swift positrons and electrons can give rise to a relatively narrow band radiation in the x-ray region. The radiation frequency is a function of velocity and gives a measure of the crystal potential, and if sufficient intensity is obtained may provide a tunable, highly directional source of x-rays.

68. PHOTOCHEMICAL, PYROLYTIC AND REACTIVE INTERMEDIATES BY ELECTRON SPIN RESONANCE 1.8 01-02
Ralph Livingston, Henry Zeldes

Short lived chemical free radicals at steady state concentration are being studied by electron spin resonance with the formation of the radicals achieved by pyrolysis of fluids. The pressurized fluid is heated as it slowly flows through the active region of the spectrometer. Temperatures to 700°C and pressures to 3000 psi are used. Primary attention is given to aromatic compounds that serve as structural models for features found in coal and in aromatic fuels. Well resolved hyperfine structure is often observed which leads to positive identification of the radicals. Chemical and physical properties of the radicals are measured including concentrations, rates of dynamic processes, and equilibria. Chemical products after pyrolysis are collected and assayed, and the results are correlated with the observed radical in order to obtain mechanistic information and kinetic constants. Currently under study are toluene and bibenzyl with hydrogen. Short lived radicals are also studied at high temperatures through the use of thermally sensitive initiators and at lower temperatures with photolytic initiation.

Chemical Physics

Combustion Sciences Department
 Sandia National Laboratories/Livermore
 Livermore, California 94550

Total \$3,600,000

69. FLAME CHEMISTRY - MODELING AND EXPERIMENT 6.0 01-02
 R. Cattolica, J. Miller, R. Mitchell,
 W. McLean, D. Stephenson

This research is aimed at providing detailed analyses of flame structure using laser probes to measure radical and major species concentrations. Finite rate chemistry models are compared with experimental results. Emphasis during the past year has been on radical chemistry, primarily OH and NH₂. Laser absorption and laser fluorescence have been used to measure OH profiles in flat flames and in surface-catalyzed combustion. Laser absorption has been used to measure NH₂ concentration and temperature in low pressure NH₃/O₂ premixed flames. The modeling work has emphasized the details of NH₃ reduction of NO and has suggested the NNH+OH product channel as important. The modeling effort includes the successful completion of a recirculating flow, finite-rate chemistry model of enclosed diffusion flames.

70. TURBULENT REACTING FLOW RESEARCH 4.0 01-02
 R. Dibble, G. Rambach, D. Hardesty

This research is directed toward an understanding of turbulent reacting flows based on application of laser diagnostic systems in the Sandia Turbulent Diffusion Flame Facility. Laser Doppler velocimetry has been used to measure axial and radial velocity components, from which mean values, turbulence intensities, turbulent kinetic energy, and higher moments were computed. Laser Rayleigh scattering was used to produce a time series of temperature data from which the probability density function was determined. This in turn allowed the mean temperature, its variance and higher moments to be computed for several positions in the flame. The Rayleigh and Doppler systems were combined to produce the first simultaneous measurement of velocity and temperature, therefore allowing construction of their cross correlations.

Combustion Sciences Department, Sandia-L, continued

71. CRF DIAGNOSTICS RESEARCH - NONLINEAR PROCESSES 3.5 01-02
 R. Farrow, L. Rahn, P. Mattern

In support of Combustion Research Facility programs, this research effort pursues the application of nonlinear optical processes for combustion diagnostics. Coherent Anti-Stokes Raman Scattering (CARS) has been improved to allow crossed-beam, phase-matched, background-rejection geometries with newly developed schemes for self-normalization such that CARS works accurately in dirty flames. Inverse Raman Scattering (IRS) has been used to provide time-averaged, space-resolved, ultra-high resolution studies of N_2 and CO in premixed flames. Our CARS work led to the discovery of a new form of Stark effect which has been incorporated into an infra-red absorption system to provide point resolution in space.

72. SOOT CHEMISTRY 4.0 01-02
 W. Flower, R. Schmieder, R. Perry,
 M. Gusinow

This research is aimed at understanding the roles of chemical precursors in soot formation. Hydrocarbon-air reactions are studied in flat flames, in flow reactors, and in combustion bombs where special diagnostics provide unique information. Laser photolysis is used on a slow-flow reactor to produce CH radicals, and a flash photolysis system is used to probe the radical-hydrocarbon chemistry. The role of superexcited acetylene in soot formation is studied using XUV photo-dissociation to produce CH^* and C_2^* . Light scattering techniques are used in a flame and in the bomb to observe soot formation, to measure particle diameter and number density, and to relate that information to a variety of experimental conditions. The origin of chemi-ionization in hydrocarbon flames and the role ions play in precursor chemistry is being studied spectroscopically, with an emphasis on C_2H^+ .

Combustion Sciences Department, Sandia-L, continued

73. CRF DIAGNOSTICS RESEARCH - ADVANCED METHODS 3.0 01-02
J. Goldsmith, M. Koszykowski,
F. Tully

This research provides the supporting analyses for the CRF diagnostic projects and investigates new methods of measuring important parameters in combustion studies. The former includes studying the effect of collisions on line widths and intensities for Raman scattering. The consequences of laser-energy deposition in chemical systems is being evaluated. This includes investigating new laser sources for kinetics studies, such as schemes for probing the electronic structure of atoms and molecules, and evaluation of a number of other processes (saturated absorption, 2-photon absorption, opto-galvanic effect, resonant ionization, etc.) for detection of trace species. Recently, two more new schemes for providing spatially-resolved absorption have been demonstrated: first, saturated absorption spectroscopy was used to detect <10 ppb of atomic sodium in a flame, with a resolution of <1 mm; second, the optical Stark effect was used to provide resolved (electronic) absorption of atomic sodium in the same flame.

74. CRF CENTRAL LASER SYSTEMS 3.5 01-02
C. Layne, C. Miller, E. Jones
J. Brannon

This project provides continued development of the two existing CRF central lasers and research in support of future major lasers. The tunable dye laser, Diana, and the YAG/Glass laser, Orion, have been installed and are operational. Beam delivery and control throughout the laboratory has been demonstrated. Research for system improvement includes investigating phase-conjugation techniques to allow higher repetition of Orion, frequency doubling Orion and Diana to obtain radiation from 240 to 370 nm, mode-locking Diana to obtain subnanosecond pulses, and Q-switching Orion to obtain 100 nanosecond pulses. Methods of improving dye lifetime for Orion are also being studied.

Combustion Sciences Department, Sandia-L, continued

75. CRF OPERATIONS AND VISITING SCIENTIST SUPPORT 11.0 01-02
J. Marion, C. Wright, L. Parker,
M. Libkind

This task supports all phases of operating the Combustion Research Facility. This includes operation of the two central facility lasers, operation and maintenance of the CRF VAX computer and networked minicomputers, operation of the computer terminals to the Sandia central CRAY, staffing of the user's shop and chemistry lab, and maintenance of the laboratory safety and control system. This task also provides support for visiting scientists and transfer of technology from the CRF to users. Visitor support includes technician and engineering staff dedicated to the visitor's project, computer time, shop, purchases, etc., used directed by visitors or in support of them.

Atomic Physics

Physics Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Total \$1,569,000

76. PHOTOIONIZATION-PHOTOELECTRON RESEARCH 3.6 01-03
J. Berkowitz

The goal is to understand the electronic structures of atoms and molecules, and their ions, by observing the interaction of vacuum ultraviolet radiation with various species and interpreting the dynamical results of this interaction. This past year has seen a significant extension of our knowledge concerning the photoionization of open-shell atoms by obtaining the photoelectron spectrum of atomic tellurium and the wavelength-dependent relative photoionization cross sections of atomic iodine and tellurium. The irreducible tensor angular momentum coupling scheme introduced earlier to explain the atomic halogen branching ratios also rationalizes the atomic tellurium results. The wavelength-dependent measurements exhibit many resonances. These have been assigned, and provide an invaluable test for ab initio theories of photoionization of open-shell atoms. Molecular ion structures have been examined by several approaches, including Franck-Condon factor analysis of photoelectron spectra, ionic model calculations and photodissociative ionization. Using the latter technique on NH_2OH , we deduce that HNO^+ is more stable than NOH^+ by ~ 0.65 eV.

77. BEAM-FOIL RESEARCH AND COLLISION 5.6 01-03
DYNAMICS OF HEAVY IONS
H. G. Berry

The work in atomic structure using fast-ion beams is aimed principally at improving our understanding of relativistic and quantum-electrodynamic effects in heavy ions. Systems with only a few (1-4) electrons are being studied to test precise ab initio 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 molecular and atomic ions in solids.

Physics Division, ANL, continued

78. THEORETICAL ATOMIC PHYSICS
K. T. Cheng

01-03

The work in theoretical studies of atomic structure is aimed mainly at improving our understanding of relativity and many-electron correlation effect in atomic processes. A multiconfiguration Dirac-Fock technique is used to study discrete excitations between bound states of atoms and stripped ions. These spectroscopic data are useful not only in interpreting observed spectra, but also in plasma studies associated with astrophysics and with controlled fusion research. Important advances have been made in the theoretical understanding of low-energy atomic photoionization in rare gas atoms using the relativistic random-phase approximation (RRPA). The validity and limitation of this technique will be further examined. Generalization of this technique to include multiconfiguration ground states, and eventually to open-shell systems is in progress. A powerful ab initio method in studying autoionization resonances and high Rydberg states is achieved by combining the RRPA with the multichannel quantum-defect theory. This method is applied to the study of window resonances in rare gases and Rydberg series in the Ne sequence.

79. HIGH-RESOLUTION LASER-rf SPECTROSCOPY
WITH ATOMIC AND MOLECULAR BEAMS
W. J. Childs, L. S. Goodman

3.6

01-03

In this program cw laser fluorescence spectroscopy and laser-rf double-resonance techniques are used for the high-resolution study of atomic and molecular beams. In the past year, the emphasis has been on the systematic study of the spin-rotation and hyperfine interactions in ground and excited electronic states of alkaline-earth monohalide radicals. Even though these molecules are the direct analog of alkali atoms (their molecular properties result from a single outer electron), their hyperfine structure is not yet understood even qualitatively and they are being intensively studied in a number of laboratories around the world. The extremely high resolution of the molecular-beam, laser-rf, double-resonance technique is now making it possible to collect previously unobtainable types of data that will, with more sophisticated calculations, lead to an understanding of these small molecules. Construction of a low energy (~ 500 eV) source for similar studies of atomic and eventually molecular ions is underway.

Physics Division, ANL, continued

80. DISSOCIATION AND OTHER INTERACTIONS OF ENERGETIC MOLECULAR IONS IN SOLID AND GASEOUS TARGETS 6.4 01-03
 D. S. Gemmell, E. P. Kanter

Argonne's 4-MV Dynamitron accelerator is used to study the interactions of fast (MeV) molecular ions with matter. A unique feature of the apparatus is the exceptionally high resolution (0.005° and 300 eV) in angle and energy obtained in measuring dissociation fragments. The apparatus also permits the coincident detection of up to three dissociation fragments. The work has two main objectives: (a) a general study of the interactions of fast charged particles with matter, but with emphasis on those aspects that take advantage of the unique features inherent in employing molecular-ion beams (e.g., the feature that 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) and (b) a study of the structures of the molecular ions that constitute the incident beams. Precise measurements on the energies and angles of the breakup fragments produced when fast molecular ions dissociate in foils and gases show promise of providing new information on the structures of the molecular ions themselves.

81. INTERACTION OF ENERGETIC PARTICLES WITH SOLIDS 0.4 01-03
 M. S. Kaminsky

It is the main goal of these studies to determine how well-characterized surface regions of lattices with (1) a defined low degree of lattice damage and low gas content, or with (2) a high degree of lattice damage and a high gas content caused by trapping of the incident ions (e.g., H^+ , D^+ , $^4He^+$) will affect the basic mechanisms of such fundamental atomic processes as ion/atom reflection, secondary ion and electron emission, atom/molecule release by sputtering, and the energy loss mechanisms (electronic and nuclear) and charge states of particles penetrating through a lattice and escaping from it. Information of this type is practically nonexistent for light-ion bombardment of solids. However, such information is of significant importance for (a) a better understanding of atomic collision processes, (b) for an analysis of older data which showed in some instances a significant scatter and may have been influenced by lattice damage and incident-ion trapping, and (c) for such practical applications as fusion plasma impurity control and accelerator technology.

Physics Division, ANL, continued

82. MÖSSBAUER EFFECT RESEARCH 0.4 01-03
G. J. Perlow

The effort during the last year has been mainly the study of gamma-ray quantum beats and their applications. Quantum beats are an individual photon effect, in which the photon amplitude is modulated at a radio frequency. This is obtained by filtering frequency-modulated quanta through a resonant medium. The frequency modulation is produced by vibrating a Mössbauer source piezoelectrically. The amplitude modulation is detected as a periodic alteration in the counting rate. Its harmonic composition is extremely sensitive to the energy difference between the gamma-ray energy and that of the resonance in the medium. This is the basis for application of quantum beats. Work is being done on the theory of the process and on improvements to the technique.

Atomic Physics

Physics Department
 Brookhaven National Laboratory
 Upton, New York 11973

Total \$185,000

83. ATOMIC PHYSICS RESEARCH

2.9

01-03

K. W. Jones and B. M. Johnson

Heavy ion beams from the Brookhaven Tandem Van de Graaff Facility are used for experiments in beam-foil spectroscopy and x-ray production. The beam-foil experiments concentrate on measurements of spectra and lifetimes of resonance transitions in the region from 5-50 nm for elements such as Ti, Fe, and Mo which are important in laboratory and astrophysical plasmas. Mechanisms for producing x rays in heavy ion-atom collisions are inferred from measurements of total x-ray production cross sections and the impact-parameter and charge-state dependence of the cross sections. Apparatus for measurement of excitation and ionization cross sections in a crossed electron-heavy ion beam experiment is under construction. Experiments to extend work to the excitation and ionization of atoms and ions by photons from the National Synchrotron Light Source (NSLS), are being designed.

Atomic Physics

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total \$450,000

84. ATOMIC PHYSICS
R. Marrus

6.3

01-03

The primary concern of this project is the atomic physics of highly-stripped heavy ions. Spectroscopic measurements in the VUV and X-ray regions are designed to test theories of relativistic effects and quantum electrodynamic effects and to provide data useful in the study of laboratory and astrophysical plasmas. Scattering measurements are concerned with electron capture and loss to continuum states. These measurements will test a theory based on the second Born approximation to explain a strong asymmetry in the cusp observed when the electron velocity and the ion velocity are equal. An ion trapping technique is being applied to measurements of charge-capture cross-sections of highly-ionized, low energy (<20 eV) ions. Measurements in this regime of high ionization state and low energy have heretofore not been possible with existing techniques. In a separate experiment, measurement of the parity-violating electron-nuclear interaction in atomic thallium is being pursued using ultraviolet lasers.

Atomic Physics

P Division
 Los Alamos National Laboratory
 University of California
 P. O. Box 1663
 Los Alamos, New Mexico 87545

Total \$85,000

85.	RADIATION FROM A HIGH TEMPERATURE PLASMA SEEDED WITH HIGH-Z ELEMENTS	1.0	01-03
	L. A. Jones		

The goal of this experiment is to study the atomic physics and photon flux transport which occurs in a hot, dense plasma. This study requires the development of a hot dense plasma source, and diagnostic techniques to investigate this source. In this experiment a large axial current is passed through a hollow cylindrical jet of gas, causing it to collapse due to its self magnetic field. The large kinetic energy of collapse is converted to thermal energy when the plasma reaches the axis. The resulting pinched plasma will reach unusually high densities and temperatures. This plasma, which is surrounded by vacuum, can be seeded with high-Z elements, providing a unique spectroscopic source. Diagnostics currently being developed include 1) x-ray spectroscopy which will yield information of the electron temperature, and 2) infrared measurements to provide optical depth information and to study anomalous emission at the plasma frequency resulting from nonlinear wave-wave and wave-particle interactions.

Atomic Physics

Physics Division
 Oak Ridge National Laboratory
 P. O. Box X
 Oak Ridge, Tennessee 37830

Total \$875,000

86. THEORETICAL ATOMIC PHYSICS 1.0 01-03
 R. L. Becker

Theoretical models and detailed calculations are made for atomic collision and radiation processes and for atomic structure properties. Specific topics are chosen primarily for their importance to the fusion energy program and to accelerator-based experimental research, and with regard for opportunities to advance the fundamental theory. This year calculations are being made on the following subjects: 1) dielectronic recombination (in support of the new ORNL merged beam experiment), 2) electron inelastic scattering followed by autoionization (being measured at ORNL with crossed beams), 3) intensity distributions of x-ray satellites produced by collisions with multiply charged ions, 4) the coupled-channels treatment of ion-atom collisions, 5) the classical trajectory Monte Carlo model of ion-Rydberg atom collisions, 6) the Bloch equations for multidegenerate two- and three-level masers, and 7) quantal and classical treatments of infrared multiphoton dissociation of triatomic molecules.

87. MERGED ELECTRON HEAVY ION BEAMS 1.2 01-03
 P. D. Miller, W. B. Dress,
 P. F. Dittner and S. Datz

The apparatus for the study of resonant electron capture by heavy ions has been installed and tested. Several experiments to observe di-electronic recombination (DER) in O^{5+} , Cl^{7+} , and Si^{4+} were carried out. To date, no electron capture above background (non-resonant charge pick-up from background gas) has been seen. The reasons for this lack of signal are currently being investigated. Among the possibilities are 1) actual cross sections of DER are much smaller than current estimates; 2) the overlap between the electron and ion beams is much smaller than expected; or, 3) the energy spread of the electrons is much larger than would be expected under Brillouin-flow conditions.

88. ACCELERATOR ATOMIC PHYSICS
P. D. Miller and C. D. Moak

4.1

01-03

The objective of this task 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 which is operated under the task 'EN-Tandem Operations'. Examples of subjects which have received particular attention during the past year are: 1) Resonant coherent excitation of one- and two-electron ions in planar channels; 2) Radiative electron capture and stopping power in channels; 3) Multiple electron loss cross sections of heavy ions in collisions with several atomic and molecular gas targets; 4) Coincidence studies of electron capture and loss to continuum states of projectiles; 5) Lifetime and photodetachment cross sections of He⁻ ions; and 6) Measurement of M-shell ionization cross sections and projectile K-, target M-shell vacancy sharing. New efforts are being started to study ion-ion charge exchange at keV energies and ion-atom charge exchange at very low energies.

89. EN TANDEM OPERATIONS
P. D. Miller and G. F. Wells

1.8

01-03

This facility is operated for atomic physics research investigating channeling, solid state material damage, electron ejection and capture from ion-atom collisions, and collisional phenomena with merged beams. Ion source development to increase the variety of heavy ions available also continues. Experimental programs using the Elbek magnetic spectrograph installed in FY 1981 are being developed for FY 1982. An ongoing study of changes in stress of materials under simulated radiation damage conditions is under development with the Metals and Ceramics Division.

90. COLLISIONS OF LOW ENERGY MULTICHARGED
IONS

1.0

01-03

R. A. Phaneuf and D. H. Crandall

Experimental studies of collision cross sections for multicharged ions are carried out at the lowest attainable energies. Emphasis is currently on electron capture from atomic hydrogen and on direct comparison of measured cross sections with theoretical results for energies below 1 keV/amu where the process is not amenable to simple characterization. A merged ion-atom beams approach for studies down to 1-eV relative energy is being developed which will employ a controlled energy neutral hydrogen beam merged with multicharged ions from the ORNL-PIG source. In addition, measurements with low velocity ions produced by a pulsed CO₂ laser incident on a solid are pursued with an atomic hydrogen oven gas target. The laser ion source experiments are currently producing cross sections for highly stripped ions (carbon ions up to C⁶⁺) in the energy range 10 to 500 eV/amu and providing direct tests of detailed coupled state calculations. Low energy electron capture with multicharged ions is important in magnetic fusion plasmas, astrophysics, ion source, and any recombining plasma. Present results are finding immediate application in these areas as well as in improving basic understanding of this fundamental process.

Atomic Physics

Laser Research and Development Department
 Sandia Laboratories/Albuquerque
 P. O. Box 5800
 Albuquerque, New Mexico 87115

Total \$130,000

91. MHD ATOMIC PROCESSES

1.5

01-03

A. Wayne Johnson and J. P. Hohimer

This research is directed toward the formation of a potassium atomic data base for theoretical calculations and diagnostic applications for MHD channel plasmas. The present experimental work is directed towards the measurement of the Stark broadening and shift parameters for a number of potassium transitions in the 4p-ns and 4p-nd series. A potassium-seeded wall-stabilized argon arc source is being used as an electron reservoir for these studies. The Stark broadened lineshapes are measured in absorption with a narrowband tunable dye laser. Previous measurements of the argon collisional broadening and shift parameters along with accurate temperature measurements in the arc source will be used to account for collisional and Doppler broadening in the lineshapes. In this manner, the dependence of the Stark parameters on the electron density is determined.

Chemical Energy

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total \$645,000

92. ORGANOMETALLIC COMPLEXES IN HOMOGENEOUS CATALYSIS 2.6 02-01
R. J. Angelici

Transition metal carbene complexes are implicated in several homogeneously catalyzed reactions, including the Fischer-Tropsch reaction. This program includes developing methods of synthesizing carbene complexes and exploring their reactivities. A simple method of preparing cyclic carbene complexes involves the reaction of metal carbonyls with 2-bromoethanol or 2-bromoethylamine. A series of $\text{CpFe}(\text{CO})_2[\text{carbene}]^+$ complexes, where the carbene ligand includes PhSe^- , PhS^- , PhO^- , MeS^- , and MeO^- groups, are prepared by other routes. Their reactivities span a broad range and suggest mechanisms for the interconversion of carbene and carbon monoxide ligands.

93. CHEMICAL KINETICS AND REACTIVITY OF TRANSITION METAL COMPLEXES 5.0 02-01
J. H. Espenson

Organometallic complexes and metal alkyls such as $(\text{H}_2\text{O})_5\text{Cr-R}^{2+}$, $\text{R-Co}(\text{dmgH})_2\text{L}$, and $\text{R-Rh}(\text{dmgH})_2\text{L}$ are under active investigation. The research concerns the characterization of the reactions which occur, and their kinetics and mechanisms. The major effort centers on reactions in which the metal-carbon bond is formed or broken, or in which rearrangements or transformation of the organic group, R, occur. Novel displacement processes at the metal or at the carbon by attacking free radicals are among reactions being investigated using techniques such as stopped-flow kinetics and flash photolysis. Included in this work are studies of organometallics which may represent classes of compounds thought to be important in Fischer-Tropsch reactions. Considerable effort has been devoted to the study of α -hydroxyalkyl, $\text{M-CH}_2\text{OH}$ and $\text{M-C}(\text{R},\text{R}')\text{OH}$, particularly the ease of further reaction as a function of the nature of M and of external reagents.

Ames Laboratory, continued

94. NUCLEAR MAGNETIC RESONANCE (NMR) STUDIES OF COALS AND CATALYSTS 4.8 02-01
B. C. Gerstein

Solid-state NMR techniques are used to estimate average structural compositions of the carbon skeletons in whole coals and coal-derived solids such as asphaltenes. Our work has employed heteronuclear ^1H - ^{13}C dipolar dephasing experiments to determine quaternary/tertiary ratios of both aromatic and aliphatic ^{13}C . Such information is used, along with X-ray diffraction data, to estimate the average number of polynuclear condensed rings, as well as the numbers and kinds of aliphatic side chains attached to these rings. Magnetic resonance techniques are also being applied to the characterization of other solid materials, including ^{29}Si in zeolitic catalysts and in amorphous silicon-hydrogen alloys ($\alpha\text{-Si-H}$) used in photoconversion devices, ^{113}Cd in cadmium-doped zeolites, and ^1H in $\text{YbH}_{1.92}$ by strong homonuclear decoupling to understand materials problems relating to hydrogen embrittlement.

95. PROPERTIES OF RARE EARTH ELECTROLYTES 0.1 02-01
F. H. Spedding

Work is being carried out on aqueous solutions of rare earth salts, with the goal of understanding the structure of the solutions and the degree of hydration of the metal ion. Toward these ends, several aspects are being investigated: (1) isopiestic data to determine activity coefficients for aqueous rare earth nitrates; (2) liquid X-ray diffraction studies of dilute rare earth chloride solutions; (3) Raman spectra of rare earth chloride solutions; and (4) Raman spectra of solids, especially low-frequency excitations in solids such as HoF_3 .

Ames Laboratory, continued

96. HIGH-TEMPERATURE GAS-PHASE PYROLYSIS OF ORGANIC COMPOUNDS
W. S. Trahanovsky 2.0 02-01

This research is directed toward an understanding of the fundamental thermal reactions of coal and coal-derived products. The general approach is to identify and to characterize these reactions by studying the pyrolysis of model compounds using primarily the Flash Vacuum Pyrolysis technique. Because hydroaromatic units are thought to be important structural features of coal and coal-derived products, tetralin, the simplest hydroaromatic compound, and substituted tetralins are being used as model compounds. Most of the experimental work consists of separating and identifying the pyrolysis products obtained from these compounds. From tetralin, the major products are benzocyclobutene, styrene, indene, 1,2-dihydronaphthalene, and naphthalene. Information about the formation of the various products is obtained by studying the effect of substituents. For example, substituent effects suggest that the formation of benzocyclobutene from tetralin involves the concerted loss of ethylene.

97. STUDY OF SOLID-GAS REACTIONS WHICH INVOLVE STRUCTURAL CHANGES IN THE SOLID
D. L. Ulrichson and A. H. Pulsifer 1.7 02-01

The objective of this work is to understand and describe the behavior of solid-gas reactions which have solid products with much larger volume than the solid reactant. The increased volume of the solid product closes diffusion paths for the gaseous reactant and stops the reaction at less than total conversion. The reaction of sulfur dioxide with calcium oxide (used for removal of sulfur dioxide from boiler flue gas) is an example in which only about thirty percent of the calcium oxide reacts before solid expansion halts the reaction. Previous models have concentrated on the effect of the reduced porosity which results from product expansion. Data from this project indicates that diffusion of reactant through the solid product layer is as important as pore reduction. Inconsistencies in published results for some solid-gas reactions can be explained by inclusion of this term. Further work is aimed at understanding the effect of solid expansion so that it can be predicted for new reactions.

Chemical Energy

Chemical Engineering Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Total \$340,000

98. FLUID CATALYSIS

3.8

02-01

J. W. Rathke, H. M. Feder, M. J. Chen

This research attempts to determine the mechanisms whereby organotransition metal complexes may catalyze the reactions of small molecules (e.g., CO) to form specific desired products. These reactions are studied by a combination of high pressure kinetic, tracer, spectroscopic, thermochemical, and theoretical methods. One example is the hydrogenation of carbon monoxide to form methanol, ethylene glycol, and other materials. We have proposed a consistent mechanism for this reaction based on solid experimental evidence and theoretical calculations. Currently undergoing intensive scrutiny is a novel soluble catalyst system discovered in our laboratory; it promotes the reaction of methanol with synthesis gas to form ethanol. This catalytic system operates by an unusual, selective and thus advantageous pathway. A detailed kinetic study and examination of the effects of modifying the catalyst complex are in progress. A further offshoot of this study is the discovery of the apparently pervasive ability of formate anion to donate hydride ion to transition metal carbonyl complexes. This reaction is being studied for its potential ability to make use of water as a hydrogen source in catalytic hydrogenation systems.

Chemical Energy

Chemistry Division
 Argonne National Laboratory
 9700 South Cass Avenue
 Argonne, Illinois 60439

Total \$730,000

99. INORGANIC CHEMISTRY 3.4 02-01
 E. H. Appelman, L. J. Basile,
 J. G. Malm, L. Stein

This research concerns the chemistry of reactive fluorine compounds and powerful inorganic oxidants derived from them. Studies involve both the synthesis and characterization of novel compounds and their application to other areas of chemistry. Further studies of the chemistry of the recently synthesized fluoroxysulfate ion, SO_4F^- , show that its reactions in aqueous solution can be effectively catalyzed by Ag^+ , thereby broadening its potential as an aqueous oxidant. The SO_4F^- ion also has been found to have promise as an oxidant for use in analyzing the structure of coal, as it appears to destroy the aromatic components of the coal macromolecule. Studies are underway of reactions of this reagent with organic compounds that are models for species present in coal. ESR studies are in progress to confirm the participation of free radicals in the reaction of SO_4F^- with aromatic compounds. A new means of "fixing" elemental xenon by its reaction with F_2 over SbF_5 at room temperature has been discovered and is being elucidated. A new project is underway to determine the ionization of strong acids in anhydrous HF.

100. THE CHEMICAL NATURE OF COALS AND COAL PRODUCTS 3.3 02-01
 R. E. Winans, R. Hayatsu

The goal of this program is to identify the structural units in coals as a function of their rank and maceral constituents. The approach is to degrade the coals, typically via oxidation, to compounds which can be analyzed by mass spectrometry and microwave emission spectroscopy. A systematic study of separated macerals has begun with emphasis on direct mass spectrometric analysis and oxidative degradation to elucidate structural parameters. An important discovery is the pervasiveness of aliphatics in coals containing a diversity of macerals. Synthetic coal-like macromolecules have been produced and characterized. These studies have yielded information concerning the transformation of biological precursors to coal and the role of mineral matter in that transformation. A direct method for determining oxygen on small quantities of coals and macerals is being developed using microwave plasma spectroscopy. All the information obtained on coals, maceral concentrates and oil shale kerogens is being correlated to obtain the structure-activity relationships needed to develop new coal conversion processes.

Chemical Energy

Bartlesville Energy Technology Center
P. O. Box 1398
Bartlesville, Oklahoma 74003

Total \$160,000

101. THERMODYNAMIC CHARACTERIZATION OF
CONDENSED-RING COMPOUNDS
William D. Good

3.0

02-01

Research continues on the synthesis, purification and measurement of thermodynamic properties for polynuclear aromatic hydrocarbons and their hydrogenation products and for similar compounds having nitrogen in their ring structures. These compounds are important in the processing of coal, oil shale and heavy petroleum to produce liquid fuels and chemical feedstocks. Thermodynamic measurements have been completed on 1,2,3,4,5,6,7,8-octahydroanthracene, isoquinoline and tolylphenylmethane. Computation of chemical thermodynamic functions is in progress. Measurements are in progress on 1,1'-dimethylbiphenyl, and several compounds are purified and ready for measurements. Gibbs energies of formation derived from these studies facilitate understanding of hydrocracking and denitrogenation. The data obtained also form the base for future correlations based on molecular structures. The comprehensive experimental program involves enthalpy of combustion, low-temperature adiabatic calorimetry (third-law entropy determinations), PVT relations including vapor pressure, Raman and infrared spectroscopy and molecular statistical mechanics.

Chemical Energy

Chemistry Department
 Brookhaven National Laboratory
 Upton, New York 11973

Total \$570,000

102. ORGANOMETALLICS IN HOMOGENEOUS CATALYSIS 2.0 02-01
 M. A. Andrews

This program concerns the study of transition metal organometallic chemistry and its relationships to homogeneous catalysis. Catalytic oxidations via the transition metal nitro-nitrosyl redox couple is the primary area of investigation and a new approach to industrially important catalytic oxidations has been demonstrated in which olefins and isonitriles are catalytically oxidized to ketones and isocyanates, respectively by $\text{Pd}(\text{CH}_3\text{CN})_2\text{ClNO}_2$ and $\text{Ni}(\text{PBU}_3)_2(\text{NO}_2)_2$. Future work will be directed at understanding the mechanisms of these reactions and modifying the catalysts to achieve selective, efficient epoxidation of olefins. Spectroscopic studies of organometallic complexes using inelastic neutron scattering are also included in this program. Preliminary work with a prototype molecule, $\text{CH}_3\text{Mn}(\text{CO})_5$, has demonstrated the potential of this tool for studying the structure and dynamics of homogeneous and heterogeneous catalysts. A study of the "anomalous collinearity effect" in EXAFS spectra of organometallics is also underway.

103. STRUCTURE AND BONDING IN METAL-HYDROGEN SYSTEMS 2.2 02-01
 T. F. Koetzle, M. L. Perlman,
 T. K. Sham

This effort is directed at improving knowledge about the electronic interactions among atoms in metals, alloys, and in other species such as cluster complexes and hydrides. Several experimental techniques are being employed: photoelectron spectroscopy; neutron and x-ray diffraction methods; Mossbauer spectroscopy; and extended x-ray absorption fine structure (EXAFS), an application of synchrotron radiation to determination of distances between an atom of a specifiable element and its neighbors. Data from the spectroscopic measurements are analyzed by theory in terms of valence and conduction band electronic configurations of the materials, and the development of this theoretical analysis is itself one of the objectives of the work. Among the aims of the diffraction studies are to investigate cluster compounds as models for the bonding of hydrogen atoms and small molecules to metals and metal surfaces and to relate structural results to thermodynamic properties of metal hydrides.

Chemistry Department, BNL, continued

104. MECHANISMS OF PHOTO-, ENZYME-, AND
CHEMICALLY CATALYZED CIS-TRANS
ISOMERIZATION
S. Seltzer

1.7

02-01

Cis-trans isomerization can be brought about by the application of heat, light or by catalysts. Because the physical and chemical properties of the two isomers differ, relaxation of a nonthermodynamic mixture of isomers (achieved by irradiation) to the thermodynamic mixture can result in the release of thermal or electrical energy. This cis-trans energy producing effect is utilized in biological processes such as the light-driven proton pump of Halobacteria and vision in animals. The proton pump can be utilized in a photogalvanic cell. This program includes studies of mechanisms of enzymically and chemically catalyzed and photosensitized cis-trans isomerizations and their application to the mechanisms of the proton pump.

Chemical Energy

Department of Energy and Environment
 Brookhaven National Laboratory
 Upton, New York 11973

Total \$700,000

105. HIGH TEMPERATURE CHEMISTRY 2.6 02-01
 James J. Egan

This is a study of the thermodynamic and transport properties of inorganic substances at high temperatures and attempts to explain the results in terms of appropriate atomic models. The 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.

106. CHEMISTRY AND PHYSICS OF COAL UTILIZATION 0.5 02-01
 T. Gangwer

The broad scope of the program is to contribute to the understanding of hydrogenation/dehydrogenation chemistry relevant to fuel conversion. The research is developing basic kinetic data and reaction pathway mechanisms for model organic systems. Kinetic studies of the tetralin, 9,10-dihydroanthracene and related hydroaromatic molecules are yielding mechanistic insight into these hydrogen donating systems. The rate constants for these systems are being studied as a function of temperature and heterogeneous surface. The hydrogen transfer from these donor solvent systems to model organic compounds is being investigated to determine the mechanisms that give rise to the observed products. Both the gas and liquid phase investigations are probing the influence of inert (e.g., N₂, Ar, Ne) and reactive (e.g., H₂, D₂) gases on the kinetic and equilibrium behavior. The polycyclic aromatic and hydroaromatic systems are studied at temperatures from where they first begin to show hydrogenation and/or dehydrogenation reactivity (~300°C) to temperatures just below where they begin to undergo pyrolysis (~450°C).

Department of Energy and Environment, BNL, continued

107. METAL HYDRIDES
J. J. Reilly

3.0

02-01

This program is concerned with the thermodynamic and structural properties of metal-hydrogen systems, particularly those involving intermetallic compounds. The presence of two (or more) metal components in an ordered lattice can result in anomalous behavior as compared to elemental metal-hydrogen systems. Of particular interest has been the apparent deviation from ideal behavior of certain intermetallic-hydrogen systems. It has been established that these deviations are due to a variety of factors, i.e., surface segregation effects, lattice strain and non-stoichiometry. The influence of sample history upon surface segregation effects of hydride-forming alloys is being investigated. In the case of FeTi it was shown that the surface composition can vary as a function of oxygen content and heat treatment. The change of alloy magnetic properties as a function of hydrogen content is also of interest. In this connection magnetic susceptibility measurements have shown that the difference in thermodynamic behavior of the two allotropic forms of TaV₂ is due to electronic rather than structural effects.

108. CATALYSIS
R. Sapienza

1.0

02-01

This study is currently exploring the importance of metal formates in carbon oxide chemistry. A new water-gas shift reaction pathway involving formate complexes, similar to that described for industrial heterogeneous catalysts, was found to be operative for Group 6 metal carbonyls. This has provided greater mechanistic understanding of the metal oxide catalysis of carbon monoxide and the relation between certain homogeneous and heterogeneous catalysts. Other studies have shown that metal formates may be key intermediates defining the catalytic link between carbon monoxide/water and synthesis gas chemistry. The path of formate decomposition and reduction relates methanol synthesis, water-gas shift chemistry, and Kolbel-Englehardt reactions. This connection suggests a different mechanism than has previously been proposed for carbon monoxide/water chemistry. The influence of various metals on the hydrogenation of zinc and iron formates demonstrates the importance of correlating metal-oxygen bond strengths to product distributions, a major task of this project.

Chemical Energy

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total \$110,000

109. BIOCONVERSION OF CELLULOSE 2.0 02-01
C. R. Wilke and H. W. Blanch

This project investigates primarily the enzymatic hydrolysis of biomass to hexose and pentose sugars. Basic information on the kinetics and mechanism of enzymatic hydrolysis is to be obtained. This information can then be used to develop low-cost processing schemes for sugar production. High productivity fermentations to convert these sugars to ethanol or other chemical feedstocks are being developed. Fundamental studies on yeast metabolism in high cell density cultures will be obtained. This will be combined with basic studies on ethanol separation from the fermentation broth, using novel, low-energy solvent extraction schemes.

Chemical Energy

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total \$1,020,000

- | | | |
|---|-----|-------|
| 110. HIGH ENERGY OXIDIZERS AND DELOCALIZED-ELECTRON SOLIDS
N. Bartlett | 2.6 | 02-01 |
|---|-----|-------|

The oxidative intercalation of graphite or boron nitride can generate durable and conductive (better than aluminum) salts. The chemical, stoichiometric and structural requirements for the best conductors need to be determined. Some have potential application as anodes in the electrochemical generation of strong oxidizers. The close chemical and structural relationship of some graphite salts to their protonated relatives such as $C_{24}^{3+} \cdot (SO_3F^-)_3$ and $C_{24}^+ SO_3F^- \cdot 2 HSO_3F$, raises the possibility of their facile interconversion by redox and proton transfer and their possible exploitation in cyclic energy storage. Some of the new, fluorine-rich graphite salts promise to have oxidizing potentials close to that of fluorine, yet these materials remain conducting in the ab plane. Oxidatively and reductively robust solid electrolytes are being sought with present emphasis on proton conductors and fluoride-ion conductors. The latter are needed in studies of the extent of the reversibility of the redox processes in the graphite salts but would have practical value in other electrochemical cells.

- | | | |
|---|-----|-------|
| 111. TRANSITION METAL CATALYZED CONVERSION OF CO, NO, H ₂ AND ORGANIC MOLECULES TO FUELS AND PETROCHEMICALS
R. G. Bergman | 1.8 | 02-01 |
|---|-----|-------|

The goal of this project is to improve our understanding, at the fundamental level, of the primary reaction steps involved in metal-induced transformations of small molecules (e.g., CO, H₂, and olefins) into larger organic molecules. One of the most important functions of H₂ in large-scale catalytic processes (e.g., hydroformylation, the Fischer-Tropsch reaction) is the cleavage of the final organic product from the metal center in the catalyst. For this reason, current attention is focused on reactions in which H₂ cleaves metal-carbon bonds. Cases have been found in which processes involving two metal centers, rather than just one, are important. These processes operate by first forming a metal hydride; the hydride then reacts with the metal alkyl to give the final products. A more recent study of the hydrogenolysis of a three-metal cluster complex yielded the surprising result of NMR emission, or chemically induced dynamic nuclear polarization. This finding strongly implicates the intervention of organic free radicals as intermediates in these hydrogenolysis reactions.

Materials and Molecular Research Division, LBL, continued

112. FORMATION OF OXYACIDS OF SULFUR FROM SO₂ 1.0 02-01
 R. E. Connick

The basic chemistry of sulfur dioxide and species formed from it are being investigated. The results are pertinent to the removal of sulfur dioxide from stack gases of power plants and to the behavior of sulfur dioxide in atmospheric pollution. Attention is being focused on the reactions of SO₂, HSO₃⁻ and SO₃²⁻ with various oxidizing and reducing agents and the disproportion reactions of these sulfur species. One particular reaction--the oxidation by oxygen--is being studied in detail because of its overriding importance in the practical chemistry of SO₂. The reaction is known to be a chain reaction in aqueous solution, both thermally and photochemically, but the chain carriers and mechanism are unknown. An important aspect is the pronounced effect of a wide variety of substances in either initiating or terminating the chain reaction and thus altering the rate drastically.

113. CHEMISTRY AND MORPHOLOGY OF COAL 1.5 02-01
 LIQUEFACTION¹
 H. Heinemann

This project has six tasks all of which are active. Accomplishments in fiscal 1981 include: (1) New methods for the electron microscope studies of coal allow identification and show distribution of ash particles. Large amounts of very small particles provide much surface area for potential catalytic reactions. (2) Potassium deposited on graphite surfaces promotes the steam-carbon reaction at the very low temperature of 250°C. The potassium gradually migrates into the bulk. (3) A novel organo-cobalt compound which mediates reversible cleavage of vinyl-hydrogen bond is under investigation. (4) Thermal decomposition of tetralin gives different products (less hydrogen) than surface catalysed decomposition. (5) Cobalt-molybdena-alumina catalysts are rapidly deactivated by metal deposition which plugs small as well as large pores. The metals deposited on the surface may have a catalytic activity of their own.

1 Joint program funded by Chemical Sciences and the Office of Fossil Energy.

Materials and Molecular Research Division, LBL, continued

114. SYNTHETIC AND PHYSICAL CHEMISTRY 0.6 02-01
W. L. Jolly

Atomic core electron binding energies of a wide variety of compounds are being determined by X-ray photoelectron spectroscopy. 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, such as organic groups, carbonyl groups, and nitrosyl groups. One can identify and distinguish various modes of ligand-metal bonding which 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. The same technique is being used to study the bonding in short-lived gaseous species, such as are formed in electric discharges and in certain high temperature processes.

115. METAL CLUSTER - METAL SURFACE ANALOGY 1.0 02-01
E. L. Muetterties

The objective of these studies is the elucidation of the molecular details of hydrocarbon metal surface chemistry. The results of these studies are then to be compared with the related chemistry of molecular coordination compounds and metal cluster species. The surface chemistry involves a study of simple hydrocarbons like benzene, toluene and acetylene on nickel and platinum surfaces as a function of surface crystallography and surface composition. The benzene chemisorption state on nickel and platinum is sharply differentiated from that of toluene on all surfaces. Benzene molecularly chemisorbs whereas toluene dissociatively chemisorbs to give the chemisorbed benzyl radical. This differentiation in surface chemistry particularly on atomically flat surfaces has provided a basis for a selective introduction of deuterium into the methyl groups of toluene by reaction of toluene and deuterium on flat nickel surfaces. This hydrocarbon chemistry is now being extended to the benzene precursors like cyclohexene and 1,3 and 1,4-cyclohexadiene.

Materials and Molecular Research Division, LBL, continued

116. ELECTROCHEMICAL SYSTEMS 1.1 02-01
J. Newman

This program includes investigation of fluid flow and electrochemical transport, measurement of transport properties in concentrated electrolytic solutions, analysis of mass-transfer rates and current distribution, design of practical electrochemical systems, and investigation of corrosion processes. Coupled kinetic, mass transfer, and fluid flow phenomena are investigated in semiconductor electrode systems, with emphasis on the optimization of configurational and operating parameters of liquid-junction photovoltaic cells.

117. THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE 3.8 02-01
G. A. Somorjai and A. T. Bell

The purpose of this program is to develop an understanding of the fundamental processes involved in the conversion of coal to liquid and gaseous fuels. A major part of the work is devoted to the catalytic synthesis of hydrocarbons and alcohols from carbon monoxide and hydrogen. The primary objectives of this effort are to determine the factors which limit catalyst activity, selectivity, resistance to poisoning, and the relationship between catalyst composition/structure and performance. A variety of surface diagnostic probes are utilized on both single crystal and supported catalysts to obtain detailed chemical information. In a second effort, a study is being performed to establish the reaction pathways involved in the liquefaction of coal catalyzed by strong Lewis Acids. Investigations are conducted both with coal and with model compounds containing representative organic structures present in coal.

Chemical Energy

Chemical Engineering Division
Lawrence Livermore National Laboratory
University of California
P. O. Box 808
Livermore, California 94550

Total \$160,000

119. EFFECTS OF METAL SURFACES ON
KINETICS OF HYDRIDE FORMATION
R. M. Alire and S. A. Steward

1.8

02-01

The objective of this study is to elucidate the surface chemistry of metals, alloys and especially intermetallic compounds that react extensively with hydrogen. Previous indirect evidence has shown that the condition of metal surfaces affects the reaction rate between hydrogen and the bulk material. Several metal systems, e.g., FeTi, LaNi₅, that are very reactive toward hydrogen are being examined with Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and other modern surface techniques. Examination of metal surfaces before, during, and after exposure to various atmospheres should provide insight into the activation or passivation of these metal systems to reaction with hydrogen. Methods of preventing or encouraging such passivation can then be formulated. Surface segregation, reduction or oxidation are examples of processes that will likely affect the initial reactivity.

Chemical Energy

Metals and Ceramics Division
 Lawrence Livermore National Laboratory
 University of California
 P. O. Box 808
 Livermore, California 94550

Total \$150,000

120. THERMOCHEMICAL PRODUCTION OF
 HYDROGEN FROM WATER
 O. H. Krikorian

1.3

02-01

Thermochemical cycles for hydrogen production from water are under study with objectives to (1) find new cycles that are both scientifically and economically viable, (2) improve known cycles by innovative chemical approaches, and (3) advance the knowledge on mechanisms of reactions associated with thermochemical cycles. Work on a $ZnSO_4$ subcycle, which bypasses many of the problems of H_2SO_4 -based cycles, is continuing with a study of the kinetics and mechanism of $ZnSO_4$ decomposition. The decomposition process is complex and can be dramatically influenced by particle size and heating rate. A study is also underway evaluating the electrolysis behavior of water dissolved in fused salts at ~ 650 K. An electrolyte based on partially neutralized H_3PO_4 shows particular promise for this application. The approach includes diffusing atomic hydrogen through a metallic membrane (Nb or Ta) at the cathode and allowing it to react with liquid Li to form LiH. The LiH is then thermally decomposed at ~ 1200 K to produce H_2 .

Chemical Energy

CMB Division

Los Alamos National Laboratory

University of California

P. O. Box 1663

Los Alamos, New Mexico 87545

Total \$380,000

121. SYNTHESIS OF THERMOCHEMICAL CYCLES

3.8

02-01

Melvin G. Bowman and Charles Hollabaugh

This research is directed to an understanding of the basic chemistry and engineering principles required to synthesize efficient thermochemical cycles for the production of hydrogen from water with primary heat sources such as solar thermal, nuclear fission and fusion reactors. A general objective is to establish the criteria and concepts required for evaluation of this new technology. The program consists of the identification, testing and preliminary development of candidate cycles. Cycles are identified by applying thermochemical principles and then tested by studies of reaction rates and reaction yields. Current studies include: 1) basic electrochemistry in the formation of dilute H_2SO_4 and H_2 from SO_2 and H_2O , 2) thermochemical and hybrid electrochemical cycles based on solid sulfate decomposition, 3) mixed metal sulfate-metal iodide cycles, and 4) low temperature reactions in cycles based on oxide decompositions.

Chemical Energy

CNC Division
Los Alamos National Laboratory
University of California
P. O. Box 1663
Los Alamos, New Mexico 87545

Total \$200,000

122. LABILE SO₂ COMPLEXES
G. J. Kubas

2.0

02-01

The basic knowledge of sulfur dioxide chemistry is being expanded with the goal of developing new methods for scavenging SO₂ from flue gases. A two-fold approach is being taken: (1) synthesis and characterization of new transition metal SO₂ complexes which may potentially be useful in direct regenerative scavenging schemes, and (2) studies of the reactivity of SO₂ coordinated to metal complexes in order to promote catalytic reactions of SO₂ with other abundant small molecules. A successful process could convert both SO₂ and NO_x into less harmful or useful by-products (e.g. hydrogen reduction to sulfur, nitrogen, and water). Reactions of SO₂ with metal cluster complexes and hydride complexes are being investigated in order to develop homogeneous catalytic methods. "Side-on" bonding of SO₂ is very much of interest since the sulfur-oxygen bonds are weakened and thereby activated towards further possible reactions. Also, the terminal oxygen displays considerable basicity and binding of Lewis acids to it are being studied as another means towards activating SO₂.

Chemical Energy

Mound Facility

P. O. Box 32

Miamisburg, Ohio 45342

Total \$235,000

123. FUNDAMENTAL INVESTIGATIONS OF METAL
HYDRIDES

2.3

02-01

G. C. Abell, R. C. Bowman, Jr.,
and M. P. Guse

This program is directed toward the identification and evaluation of the atomic properties which influence the characteristics of metal hydrides for potential use as chemical energy storage materials. Experimental techniques, such as NMR, cryogenic x-ray diffraction and thermal analysis, are being used to determine: 1) roles of crystal structure, composition and phase transformation in hydrogen storage and transport; 2) changes in electronic structure with hydride formation; and 3) effects of metal alloy substitution on hydride properties. Current studies involve hydrides formed from TiV alloys, LaNi_5 , CaNi_5 , TiCr_2 and TiCu compounds. Modified quantum-mechanical calculations of electronic properties of metal atom clusters containing hydrogen are being performed, currently utilizing advanced density functional theory. An alternative description of hydrogen in Group Vb metals, based on localized electronic states, is also being pursued and is helping to explain many of the anomalous properties of these metal hydrides.

Chemical Energy

Chemical Technology Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Total \$200,000

124. KINETICS OF ENZYME CATALYZED PROCESSES 2.3 02-01
 E. Greenbaum, J. Woodward

Fundamental physico-chemical studies on the conversion of light energy into chemical energy are being continued. We are studying the basic rate limiting reactions of light energy conversion by the Chloroplast-Ferredoxin-Hydrogenase (CFH) system. In particular, we have performed the first measurement of the turnover kinetics of the CFH system. For this measurement we illuminated the CFH system with saturating single-turnover flashes of light of variable repetitive frequency. This technique allows a direct and unambiguous measurement of the turnover times of the photoreactions associated with hydrogen and oxygen production. The results are most encouraging because they imply that the intrinsic kinetic rate capability of the CFH system is such that it can keep pace with the rate of incident solar quanta. In addition, glutaraldehyde-treated chloroplasts, which have been shown to have higher storage stability than their native counterparts, have been tested for their operational stability in the in vitro Chloroplast-Ferredoxin-Hydrogenase system.

Chemical Energy

Chemistry Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Total \$2,000,000

125. AQUEOUS CHEMISTRY AND THERMODYNAMICS TO 5.1 02-01
ELEVATED TEMPERATURES AND PRESSURES
R. H. Busey, H. F. Holmes,
D. A. Palmer, W. L. Marshall,
F. H. Sweeton

In this program we apply physical-chemical techniques to the study of the thermodynamics of processes in aqueous media at the temperatures and pressures encountered in energy related technologies. In order to permit predictions of chemical behavior in solution under new conditions of temperature and pressure fundamental relationships are being derived. The specific approaches emphasized are: potentiometry, conductance, calorimetry, isopiestic and phase equilibrium studies. New techniques are being developed and applied to model systems to derive a data base on the thermodynamics of solutes, and predictive capability on processes such as: ionization, association, hydrolysis, solubility, salt effects and volatility of inorganic solutes principally up to 300°C but in more limited circumstances to 800°C. Efforts are being made in many divergent applications elsewhere to model complex natural and practical processes in terms of equilibrium thermodynamic data.

126. ORGANIC CHEMISTRY AND THE CHEMISTRY OF 7.2 02-01
FOSSIL FUELS
C. J. Collins, E. W. Hagaman,
L. L. Brown, M. L. Poutsma

The current themes of this project are: (1) determination of coal structures; (2) investigation of the Na-K method for cleaving carbon-carbon bonds in coal and compounds modeling coal; and (3) elucidation of mechanisms for thermolysis of model coal structures. Application of additional resolution-enhancement techniques to CP-MAS ^{13}C NMR has allowed the identification of several specific kinds of carbon atoms both in the aromatic and aliphatic regions. This method has been illustrated by determining the action of NaK on Illinois #6 coal followed by quenching with methyl- ^{13}C iodide. The mechanisms of cleavage of the $\text{sp}^3\text{-sp}^3$ C-C bond in bibenzyl and the $\text{sp}^3\text{-sp}^2$ C-C bond in diphenylmethane were shown to be distinctly different. Thermolysis studies have focused on $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{-C}_6\text{H}_5$ and naphthols. For the former, β -scission, free-radical chain reactions for $n \geq 3$ lead to enhanced reactivity over that predicted only from C-C bond strengths; for the latter, a coupled condensation-hydrogen transfer process which produces dinaphthofurans (via binaphthols) and tetralones is being unraveled.

Chemistry Division, ORNL, continued

127. STEAM GENERATOR CHEMISTRY

0.9

02-01

W. L. Marshall, F. H. Sweeton

The objective of this program is to conduct basic research addressing some of the solution phase equilibrium and solution chemistry problems which limit power plant efficiency and capacity, principally in the steam generating stage. The specific problems can be grouped among the following: corrosion of metals of construction and the transport and deposition of dissolved components. The chemistry of the dissolved constituents, either intrinsic or introduced as an additive, which leads to corrosion, deposition or distribution to the gas phase in both nuclear and fossil fueled generators is the concern of this program. Also, because the radiation fields caused by the deposition on the primary side in nuclear plants complicate maintenance procedures and decontamination in accident situations, the chemistry of contamination (and decontamination) processes will be included. The approach will involve detailed thermodynamic studies on the constituents of interest in solution, their equilibria with solids and also their distribution to the gas phase.

128. HETEROGENEOUS CATALYSIS RELATED TO
ENERGY SYSTEMS

3.4

02-01

S. H. Overbury, P. A. Agron,
W. C. Waggener

The objective of this research is to investigate chemical bonding and structure of model catalytic surfaces, and the relationship between these properties and catalytic activity. Three complementary physical methodologies are being developed and applied to this end. The first employs angle resolved photoelectron spectroscopy to elicit information on the bonding and orientation of molecules adsorbed on metallic crystals. Emphasis has been placed on the behavior of sulfur-containing organic compounds. The second technique, angle resolved ion scattering spectroscopy, is used to determine surface structure and atomic composition, and studies of oxygen chemisorption and oxidation of metal surfaces are in progress. The third method probes the tangential forces on a metal foil caused by surface adsorption through observation of macroscopic distortions. This highly original method is used to study adsorbent-adsorbate forces (such as those induced by adsorbing H₂ on Ni) as a function of time and surface coverage.

Chemistry Division, ORNL, continued

129. INORGANIC CHEMISTRY OF HYDROGEN CYCLES 1.5 02-01
P. R. Robinson and C. E. Bamberger

The thrust of this project is the study of inorganic reactions, especially at high temperatures, that can be associated with related reactions at or near ambient temperature to form viable thermochemical cycles for splitting water. Additionally, reactions are sought that can be used for splitting CO₂. The reduced products, H₂ and CO, respectively, have a wide range of uses from being nonpolluting fuels to being major reagents in the synthesis of very important chemicals; e.g., ammonia, gasoline, methanol, etc. The results obtained to date include the discovery of several new inorganic compounds and many new reactions. The knowledge provided by the latter together with that of established reactions has been systematized into a thermodynamic-based model which is used for selecting reactions for the development of new cycles. These reactions are then confirmed experimentally in order to obtain additional information pertaining to kinetics, side reactions, etc.

130. MOLTEN SALT CATALYSTS FOR CLEAN 4.1 02-01
FUEL SYNTHESIS
G. P. Smith, A. S. Dworkin,
A. C. Buchanan, III

In this program, mechanisms are studied of molten salt catalyzed hydrogenation, hydrocracking, and simultaneous polymerization reactions of organic compounds chosen to model certain aspects of the coal structure. The important mechanisms governing the removal of organically bound sulfur and nitrogen also form part of these studies. The catalytic melts chosen for study are made up from haloaluminates or posttransition metal halides as dominant constituents. Examples of the latter are antimony trichloride and zinc chloride. The formation, stability and reactions of species important in catalytic mechanisms, such as carbenium ions, radical cations, unstable or unusual oxidation states of metals and unusual metal coordinations are studied. Direct observations of these species in the melt are made by NMR, ESR, optical spectroscopy and electrochemical methods. Reaction products are also studied by quench and work up procedure.

Chemical Energy

Chemical Technology Department
 Pacific Northwest Laboratory
 P. O. Box 999
 Richland, Washington 99352

Total \$370,000

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|--|-----|-------|
| 131. MECHANISMS OF HYDROGENATION OF COAL
J. A. Franz and D. M. Camaioni | 2.0 | 02-01 |
|--|-----|-------|

The tasks of this program are (1) to determine the structural changes in coals under conditions of flash hydroliquefaction in hydrogen donor media; (2) to determine mechanisms of hydrogen transfer during hydroliquefaction of coals and to determine sites to which hydrogen is transferred using deuterium and other labeling techniques; (3) to determine the mechanisms of formation and reactions of organic free radicals and other transient species and their roles in coal dissolution. The overall objective of the program is to gain a basic scientific understanding of the structural features of coal which control its conversion from an insoluble solid to soluble products, and to determine the relevant mechanistic pathways leading from solid coal to products. The approach of the program is to examine the products from kinetic flash hydroliquefaction of coals in deuterated or unlabeled hydrogen-donor solvents. Specific radical reactions are being studied by flash-vacuum pyrolysis of radical precursors, relative rate measurements in solution, and other methods for the study of high-temperature reactions.

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|---|-----|-------|
| 132. THERMOCHEMICAL CONVERSION OF SOLID
WASTES INTO LIQUID FUELS
P. M. Molton, R. K. Miller,
J. A. Russell | 3.2 | 02-01 |
|---|-----|-------|

To simplify the general problem of biomass liquefaction, this study is considering separately the conversion of the three major biomass components; cellulose, lignin, and hemi-cellulose. Extensive analysis of model-compound experiments is increasing our understanding of the chemical mechanisms in aqueous alkaline cellulose liquefaction. Aldol condensation and the closely related Michael reaction are important in the mechanisms leading to furans, ketones, and aromatics which together comprise 68% of the 85 compounds that we have identified by gas chromatography/mass spectrometry as products of cellulose liquefaction. Pretreatment of cellulose with ozone is being examined and work with lignin is beginning. For comparison, the aqueous alkaline liquefaction products of several different types of biomass are being studied. These types of biomass include peat, hops residues, sewage sludge, and pine branches.

Chemical Energy

Physical Sciences Department
Pacific Northwest Laboratory
P. O. Box 999
Richland, Washington 99352

Total \$90,000

133. KINETIC AND MECHANISTIC STUDIES ON
THE HYDROGENATION OF HETEROCYCLIC
NITROGEN COMPOUNDS
J. R. Morrey

0.7

02-01

There is a critical need to better understand the chemistry of nitrogen heterocyclics as they are hydrogenated for several important reasons: they are principal constituents of aliphaltenes and preasphotenes (intermediates in conversion of coal to oil asphaltenes preaspholtene products); they are probably major contributors to the resistance of coal to dissolution; they cause high emission of NO_x during combustion; they poison hydrocracking catalysts; and they are implicated in the carcinogenic and mutagenic properties of refined coals. The purpose of this research is to determine the fundamental kinetics and mechanisms which govern the hydrogenation reactions of individual nitrogen heterocyclics isolated from raw coals. Compounds are first separated from raw coals and identified, then representative models are studied in a specially designed mass spectrometric system under non-isothermal conditions to obtain fundamental data which are used to delineate chemical mechanisms.

Chemical Energy

Radiation and Surface Physics Research Department Total \$50,000
Sandia National Laboratories/Albuquerque
P. O. Box 5800
Albuquerque, New Mexico 87115

135. REACTION KINETICS OVER SINGLE CRYSTAL 1.4 02-01
 CATALYSTS
 D. Wayne 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 probes. 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 specially built ultra-high vacuum apparatus allowing both kinetic measurements and surface analysis. Virtually identical kinetic parameters have been found for the methanation reaction over single crystals of nickel and ruthenium as have been measured for high surface area nickel and ruthenium process catalysts. The poisoning of a single crystal methanation catalyst by electronegative adatoms has also been studied and a correlation has been found between the electronegativity of the impurity atom and its catalytic poisoning ability. This work is being extended to establish whether other catalytically interesting reactions can be modeled using single crystal materials.

Chemical Energy

Research Division
 Solar Energy Research Institute
 1617 Cole Boulevard
 Golden, Colorado 80401

Total \$50,000

136. BASIC RESEARCH IN SYNTHESIS AND CATALYSIS	0.5	02-01
J. C. Smart, D. L. DuBois, and		
C. J. Curtis		

This basic research program 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. Exploratory synthesis of new dinuclear complexes of the early transition metals with the bridging fulvalene ligand is underway, along with the designed organic synthesis of new bridging s- and as-indacene ligands. Spectroscopic and photochemical studies of the Group VIII metallofulvalene complexes is contributing to an understanding of their electronic structures and the potential utility of their low lying excited states. Photoelectrochemical N_2 -fixation studies involve the synthesis and characterization of surface bound phosphine molybdenum(0) dinitrogen complexes. These include the preparation of new pendant tridentatephosphine polymethacrylamide polymers, together with electrochemical and FT-infrared studies.

Separations

Ames Laboratory

Iowa State University

Ames, Iowa 50011

Total \$160,000

137. HYDROMETALLURGICAL PROCESSING

2.5

02-02

Renato G. Bautista

The development and understanding of hydrometallurgical methods of recovering metals to include dissolution (leaching), separation and concentration (ion exchange, solvent extraction, and membrane separation) and metal reduction from solutions (cementation, precipitation, and electrolysis) based on the equilibria, mechanisms, kinetics, and transport properties of the chemical reaction system are the related activities which are the principal objectives of this research program. Helgeson's partial equilibrium model has been successfully applied to the chalcopyrite-ferric sulfate-sulfuric acid system to predict the concentration of the effluent copper leached solution and the precipitation of iron in the form of jarosite from the analytical concentration of the influent leach solution. The insight gained from this chemically based model is applicable to both the copper mine waste dump and to the in-situ leaching of copper ores where control of the chemical reactions can only be made by changes in the influent leach liquor. This method is being extended to the uranium dioxide-ferric sulfate-sulfuric acid system.

138. ION EXCHANGE METHODS FOR SEPARATIONS

1.3

02-02

J. E. Powell

This research is directed toward developing methods of separating trivalent actinons from associated fission-produced elements in that third of nuclear reactor wastes that can be partitioned handily by simple precipitation as mixed oxalates. A separation factor of 1.7 (between Am and the first lanthanons to elute from a cation-exchange column) has been demonstrated recently with bis-(2-aminoethyl)ether-N,N,N',N'-tetraacetate (EEDTA) as the eluant. Cm, Bk and Cf eluate ahead of Am. Analogues of EEDTA in which the ether-O is replaced by amino-N are being investigated as potentially more selective An-Ln ligands than EEDTA. A SF of 1.7 or more between any An and any Ln ensures the feasibility of isolating individual Ans from nuclear wastes by the technique of displacement chromatography to permit utilization, destruction by transmutative burn-up, or safe disposal by burial in some geologic repository in a stable discrete mineral form.

Separations

Chemistry Division Total \$900,000
 Argonne National Laboratory
 9700 South Cass Avenue
 Argonne, Illinois 60439

139. SEPARATION SCIENCE RELATED TO FOSSIL FUEL TECHNOLOGIES 3.3 02-02
 E. P. Horwitz, G. R. Dyrkacz,
 C. A. A. Bloomquist

This research program has as its objectives the development of new and improved physical separation processes that are applicable to the processing and utilization of oil shale and coal. A rapid and efficient method for the separation of coal macerals based on their differences in densities has been developed. The separated macerals are being used to study their physical properties with the objective of finding new properties on which to base new and improved separation techniques. The purified macerals are also being used in the investigation of their structures and chemical properties. Studies on oil shale are directed at measuring the extent to which the organic constituents are bonded to the inorganic mineral matrix. Wet grinding combined with surfactant adsorption and preferential wetting are being investigated as a possible method for enriching the kerogen from Green River and Devonian shales.

140. CHEMICAL SEPARATION SCIENCE RELATED TO NUCLEAR AND HYDROMETALLURGICAL TECHNOLOGY 7.4 02-02
 E. P. Horwitz, D. Kalina, L. Kaplan,
 G. Mason, P. G. Rickert

This research program is involved with basic studies on the complexation of metal ions by organic extractants and on the interfacial mass transfer of metal ions from an aqueous to an organic environment. Knowledge gained from the basic studies is applied to the development of new and improved separations methods of importance in nuclear fuel reprocessing, nuclear waste processing, and the recovery of strategic metals which have rather limited domestic supplies. This program is also involved with the development of more energy efficient separation procedures which may be applied to commercial scale hydrometallurgical processing. The major areas of investigation are: (1) the synthesis and characterization of new extractants for metal ions, (2) the kinetics and mechanisms of interfacial mass transfer, and (3) the physical chemistry of solid supported liquid membranes.

Separations

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total \$125,000

141. LASER-INDUCED REACTIONS FOR
ISOTOPE SEPARATION
R. E. Weston

1.6

02-02

The photochemical separation of isotopes is possible because atomic and molecular energy levels depend on atomic masses. The difference in levels permits the selective photoexcitation of a single isotopic species, which either decomposes or can be removed by a chemical or physical process leading to an isotopically enriched product. To provide information basic to laser isotope separation, unimolecular reactions, bimolecular reactions, and photodissociation processes of vibrationally excited molecules are being investigated for the selective removal of photoexcited molecules. Currently under investigation are: (i) the IR multiphoton dissociation of CF_3Cl , using IR chemiluminescence from vibrationally excited HCl and HF as probes; and (ii) the photochemistry and photophysics of highly vibrationally excited SO_2 . This may be one of the first observations of "inverse electronic relaxation", in which vibrational energy is converted to electronic energy.

Separations

Department of Energy and Environment
 Brookhaven National Laboratory
 Upton, New York, 11973

Total \$145,000

142. CYCLIC SEPARATIONS PROCESS RESEARCH
 F. B. Hill

1.3

02-02

The purposes of this program are to obtain an understanding of the characteristics and basis of operation of cyclic separation processes as a class, and to explore the feasibility of using these processes to perform specific separations important in the energy field. The cyclic processes of interest include pressure and temperature swing adsorption, parametric pumping, cycling zone adsorption and various forms of preparative chromatography. Applications presently under study involve isotope separations of concern in nuclear technology, specifically tritium removal from process effluents and heavy water production, and helium extraction from natural gas. Future work will include applications such as hydrogen recovery and purification, and ion exchange separations useful in nuclear waste management. Elements of the program include development of the theory of cyclic processes, measurements of equilibrium and kinetic properties of selected fluid-solid separation systems, measurement of the characteristics of cyclic separation processes employing these systems, and process design and evaluations studies.

Separations

EG&G Idaho, Inc.
Idaho National Engineering Laboratory
P. O. Box 1625
Idaho Falls, Idaho 83415

Total \$50,000

143. SELECTED ELEMENTAL SEPARATION STUDY 1.0 02-02
L. D. McIsaac and J. D. Baker

The extraction behavior of TcO_4^- and Pd(II) from aqueous HNO_3 was studied using dihexyl N, N-diethylcarbamoylmethylphosphonate (DHDECMP). Distribution ratios were studied as a function of contact time, concentration of solute, acid, and extractant, and extraction temperature. Extraction measurements of TcO_4^- were also made using H_2SO_4 in the aqueous phase. It was found that the extractant dependency for TcO_4^- is third power. Distribution measurements for TcO_4^- as a function of temperature in the range of 0-50°C led to a calculation of the thermodynamic quantity ΔH . A third power extractant dependency for Pd(II) is suggested but is not strongly corroborated. Interpretation of Pd(II) data was hindered by slow kinetics (approximately 1 hr to reach equilibrium) and variations in distribution ratios with aqueous Pd(II) concentration.

Separations

P Division Total \$150,000
 Los Alamos National Laboratory
 University of California
 P. O. Box 1663
 Los Alamos, New Mexico 87545

144. THE FORMATION AND PROPERTIES OF COMPLEXES 1.0 02-02
 OF HELIUM AND HYDROGEN ISOTOPES
 R. D. Taylor

The experimental properties of a newly discovered metastable bound-state formed between a noble gas and hydrogen are being investigated. Tritium, the heaviest isotope of hydrogen, is radioactive and decays with a half life of 12.3 years, ultimately producing a pair of helium-3 atoms and a concomitant pressure increase in a fixed volume of gas. However, at a temperature of about 21 K the ^3He formed in liquid T_2 is retained in the liquid in an amount far exceeding the ordinary solubility, suggesting that a metastable helium-tritium molecular complex is formed. Experiments so far have shown the complex is virtually stable in liquid or solid tritium and is definitely unstable in gaseous tritium. The complex exhibits little, if any, magnetic behavior and has an effective vapor pressure less than that of the tritium host liquid. The electrical conductivity of liquid T_2 has been observed to increase with time (concentration of an ionic complex). Several models for the observed behavior are being examined.

Separations

Mound Facility

P. O. Box 32

Miamisburg, Ohio 45342

Total \$710,000

145. ISOTOPIIC EXCHANGE RATES IN H-T AND D-T
MIXTURES

0.8

02-02

G. T. McConville

The purpose of this study is to obtain a more complete understanding of gaseous mixtures of hydrogen isotopes, in particular, the mechanism for isotopic exchange in such mixtures. Such information is necessary to support design criteria for fuel handling systems in the controlled thermonuclear fusion power programs. The high temperature mixing chamber and supply system has been installed in a glovebox and is connected through a capillary sampling system to a mass spectrometric analysis laboratory. Starting at 300K exchange rates are being measured as a function of density, T₂ concentration and He₃ concentration. There are indications that the presence of inert gas impurities in rather small concentrations affects the exchange rates.

146. ISOTOPE SEPARATION RESEARCH AND
DEVELOPMENT

3.0

02-02

W. M. Rutherford, B. E. Jepson,
and E. D. Michaels

This program is concerned with the investigation of chemical exchange and liquid phase thermal diffusion as techniques for stable isotope separation. The primary objectives of the chemical exchange work are to find significant isotope effects in metal isotope exchange between aqueous and organic ligand phases and to develop closed cycle methods of refluxing chemical exchange systems with oxidation state changes between the exchanging species. The liquid thermal diffusion work is directed, in part, toward developing a basic understanding of the behavior of liquid phase thermal diffusion columns and, in part, toward gaining experimental information about the isotopic thermal diffusion factor in the liquid phase.

Mound Facility, continued

147. MOLECULAR SCIENCE RESEARCH

2.8

02-02

W. L. Taylor, G. T. McConville,
and R. W. York

The objective of this program is to conduct basic research on the fundamental properties of isotopes and atomic or molecular species which are pertinent to the development or improvement of new or existing technologies. Experiments are being conducted to measure the total elastic scattering cross section of selected gases at thermal energies with supersonic molecular beams. The thermodynamics of the thermal diffusion process is under investigation and mass diffusion coefficients of gas pairs are being determined over an extended range of temperature. The liquid and solid properties of the hydrogen isotopes and their spin isomers are being investigated by vapor pressure and heat capacity measurements. A theoretical study is underway to characterize the angle dependent intermolecular potential for the hydrogen isotopes. Experimental data resulting from this program, along with other available data, are used to probe the fundamental molecular interaction, to ascertain accurate intermolecular potentials.

Separations

Chemical Technology Division Total \$1,950,000
 Oak Ridge National Laboratory
 P. O. Box X
 Oak Ridge, Tennessee 37830

148. CHEMICAL ENGINEERING RESEARCH 4.5 02-02
 (CHEMICAL SCIENCE)
 J. M. Begovich, S. D. Clinton,
 J. S. Watson

Fundamental chemical engineering studies of separation techniques explore new concepts and improved understanding of conventional separation techniques. A rotating annular chromatograph is being studied for separation of several components continuously. The chromatograph is capable of either isocratic or gradient elution operation, and scale-up parameters are explored using an example ore liquor. The continuous pressurized chromatograph is receiving favorable reception as a new technique for performing difficult chemical separations, eventually on an industrial scale. The operating characteristics of high-temperature slagging processes are being studied to improve techniques for recycling scrap metals. An experimental study is being initiated to evaluate sorption in expanded beds stabilized by electric fields. The electric field restricts movement of solids and allows high concentration gradients desirable for efficient absorption.

149. FUNDAMENTAL CONCEPTS FOR RESOURCE 4.0 02-02
 RECOVERY
 R. M. Canon, A. D. Kelmers

This basic research investigates separation techniques to recover useful materials from wastes and novel low-grade ores. The techniques will be useful for both pollution control and conservation of resources. New techniques have been studied which recover aluminum, iron, and other metals from coal fly ash and also remove and isolate toxic trace components that cause environmental hazards after disposal. An attractive technique involves extracting half or more of the available aluminum from the ash with hydrochloric acid. Current studies characterize ash and extraction residue, evaluate extraction kinetics, and investigate separation of extracted components. Other approaches are capable of recovering up to 95% of the aluminum from any ash, but they consume reagents such as flue gas desulfurization sludge and require more energy.

Chemical Technology Division, ORNL, continued

150. FUEL CYCLE CHEMISTRY 3.7 02-02
R. L. Fellows, D. J. Pruett,
L. M. Toth

Chemistries of actinides and fission products are investigated with respect to optimizing separations, minimizing wastes, and discovering new separation processes. This program addresses fundamental characteristics of important factors in fuel recycle; these presently include: (1) solids formation in reprocessing and waste solutions; (2) actinide and fission product ion complexation with solvent degradation products; (3) plutonium polymer formation; (4) solvent extraction kinetics; (5) chemistry of specific fission products - ruthenium, technetium, and tellurium; and (6) photo- and associated chemistry of the actinides and fission products. Both the concentration and the nature of the species in question are determined in order to describe the basic physical chemistry of the system. Standard analytical techniques of spectrophotometry, electrochemistry, chromatography, and tracer analysis are combined with α -, β -, and γ -containment techniques to study realistic fuel recycle systems over a wide range of experimental conditions.

151. TRITIUM SEPARATION TECHNOLOGY 1.5 02-02
P. W. Fisher, J. B. Talbot

This research is directed at techniques for separating tritium in fusion and fission reactor systems. Methods for removing tritium from molten lithium, the most promising breeding material for fusion reactor blankets, are being studied. The tritium recovery technique must be particularly efficient to maintain a low inventory of residual tritium in the blanket. Experiments indicate that yttrium sorbents can remove tritium from lithium effectively, and liquid and solid phase mass transfer resistance to sorption are being evaluated. Effects of yttrium impurities and surface area on absorption and desorption rates are being investigated. Additional studies are measuring equilibrium adsorption isotherms and diffusivities for hydrogen isotopes in adsorbents which are important to design of systems to separate unburned tritium fuel from fusion reactors.

Chemical Technology Division, ORNL, continued

152. SEPARATIONS SYSTEMS RESEARCH
W. J. McDowell

6.0

02-02

The objective of this program is to develop and to understand the scientific basis for new and improved chemical and physical separations methods. The scope includes applications to hydrometallurgy, fossil fuel conversion, nuclear fuel reprocessing, waste treatment, and special chemical analysis. Present studies include: (1) the investigation of the use of macrocyclic compounds (crown ethers, thio crown ethers, and porphyrins) as size-selective coordinative synergistic agents in liquid-liquid extraction systems. (2) the behavior of bis(2-ethylhexyl)sulfoxide in the extraction of uranium, plutonium, and fission products from nitrate solutions; (3) the chemical and physical basis of interfacial phenomena such as emulsion stability and the formation of stable interfacial solids in extraction systems; (4) the use of separations procedures in conjunction with Photon Electron Rejecting Alpha Liquid Scintillation (PERALS) spectrometry for alpha assay in our own laboratory and elsewhere; and (5) the assembly and maintenance of the Separations Science Data Base.

Separations

Chemistry Division
 Oak Ridge National Laboratory
 P. O. Box X
 Oak Ridge, Tennessee 37830

Total \$450,000

153. FUNDAMENTALS OF SEPARATIONS CHEMISTRY	2.3	02-02
C. F. Baes, Jr., J. H. Burns, F. Dowell		

The purpose of this program is to obtain basic information about solvent-extraction systems that may lead to improved processes for the recovery of strategic metals. For the multicomponent systems involved in various separation processes, theoretical modeling is being used to explain and predict the effects of different functional groups and chain geometries of component molecules on thermodynamic properties, especially phase behavior. Measurement of densities of mixtures of long-chain alkanes and determination of activity coefficients by gas-liquid chromatography are providing experimental data for correlation with theory. Determinations of the structure of extraction complexes of uranium by x-ray diffraction are being used to investigate the mechanism by which these metal ions are chemically bound and extracted. The requirements of molecular shape, charge, and coordination which must be met in order to have an effective extractant are being ascertained. All of these studies are focused on behavior at the molecular level and are expected to provide guidelines by which a more systematic selection or design of extractants for specific applications can be made.

154. FLOW THROUGH POROUS BODIES	1.1	02-02
S.-Y. Shiao, J. S. Johnson		

Processes involving fluid flow through porous media which have been of interest include column chromatography; mixing of fluids of different density and viscosity in passage through porous solids; filtration; membrane transport; and reactions in suspensions and fluidized beds. At present, emphasis is on adsorbents stable in difficult environments and on their preparation in forms suitable for column operation. Many substances of attractive selectivity and adsorptive capacity and also able to withstand radiation, elevated temperatures, and aggressive chemical media are difficult to prepare in particles of size distribution and resistance to dispersion favorable for chromatography. Impregnation of porous materials having good flow characteristics can obviate this problem. At present, emphasis is on ion-exchange properties of hydrous Zr(IV) oxide as a function of solution composition and pH and on development of procedures for loading it into the pores of activated carbon particles. This hydrous oxide itself has extremely interesting ion-exchange properties, and it can also serve as a base for mixed oxide exchanges, for example with P(V), Mo(VI), and W(VI), of remarkable selectivities.

Chemistry Division, ORNL, continued

155. MOLTEN SALT PROCESSES FOR HIGH LEVEL
RADIOACTIVE WASTE 1.0 02-02
F. J. Smith

New aspects of the basic chemistry that relates to high-temperature non-aqueous methods of nuclear waste management are being studied with particular emphasis on obtaining critical materials. Molten salt/liquid metal systems are chosen for such tasks because of their inherent radiation and proliferation resistance. Separation processes are sought for (1) partitioning nuclear waste, (2) providing methods for safer storage techniques, and (3) recovering beneficial nonradioactive fission products. Separation factors greater than 10^6 for palladium and rhodium from ruthenium have been determined which indicate the feasibility of isolating significant quantities of nonradioactive palladium and rhodium from short-cooled fuel. Raman and thermodynamic studies of fission products and transuranium elements in molten salt and liquid metal media are emphasized.

Separations

Chemical Technology Department
Pacific Northwest Laboratory
P. O. Box 999
Richland, Washington 99352

Total \$75,000

156. PYROCHEMICAL SEPARATIONS
L. L. Burger and L. G. Morgan

0.6

02-02

The task involves the application of pyrochemical techniques to chemical separations in the nuclear fuel cycle. Both nuclear fuel reprocessing and treatment of nuclear wastes can be facilitated by separation of the constituents into chemical families where the forms and chemical behavior are unique. Pyrochemical processes remove the complication of the water molecule which largely determines conventional chemical behavior. Laboratory studies emphasize work in two areas: molten nitrate salt systems and glass slag reductions. The first involves a study of the chemical behavior of elements and families of elements in molten nitrates. The second examines oxidation-reduction reactions accompanied by distribution of elements and compounds between a molten metal and a second liquid phase, a "flux" or solvent. Partitioning is influenced by varying the redox potential of the basic chemical step and by varying the acidity or basicity of the flux.

Analysis

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total \$760,000

157. ANALYTICAL SPECTROSCOPY 5.5 02-03
V. A. Fassel, A. P. D'Silva, R. N.
Kniseley, J. F. McClelland, W. J. Haas

This effort is devoted to the systematic observation of spectroscopic phenomena with the ultimate goal of utilizing these observations for devising new spectroscopic analytical concepts that offer promise of solving singularly difficult analytical problems that either exist now or are likely to arise in the future in the various fields of energy generation, the conversion of coal to liquid and gaseous fuels, solid state materials research and in environmental pollution. Emphasis is being placed on: (a) novel applications of electrical plasmas as vaporization-atomization-excitation-ionization sources for analytical atomic emission and fluorescence spectroscopy; (b) analytical applications of highly selective energy transfer processes from x-ray and laser beams to trace constituents in solid materials, leading to optical emission, e.g., x-ray or laser excited optical luminescence; (c) selective energy transfer from gaseous metastable species to trace level gaseous organic or inorganic constituents, with the intent to devise new analytical concepts; and (d) photoacoustic spectroscopy and detection analytical techniques.

158. ANALYTICAL SEPARATIONS AND CHEMICAL ANALYSIS 2.6 02-03
J. S. Fritz

Major research is concerned with development and analytical applications of a new method of ion-exchange chromatography, with methods for concentration and analysis of organic pollutants in aqueous samples, and with new chelating reagents and resins for concentrating selected metal ions from water. The new method of ion-exchange chromatography is particularly important in the analysis of common anions. For example, in power generation plants stress corrosion cracking of turbine blades by impurities in the steam is a major problem. Our analytical method provides a simple means of monitoring corrosion-forming anions such as chloride and sulfate at the low parts per billion concentration. Our research has produced analytical procedures for determining organic pollutants in water that have proven absolutely vital for the analysis of many specific environmental samples.

Ames Laboratory, continued

159. ANALYTICAL MASS SPECTROSCOPY 2.2 02-03
H. J. Svec, R. J. Conzemius

This project involves the application of mass spectrometry to analytical problems involving organic, conducting, semiconducting and insulating solids and the organic constituents in complex mixtures. The basic science is emphasized. Of particular concern in GC/MS studies of complex mixtures of organic compounds is the ambiguous identification of individual constituents, often due to the lack of chemical information needed to support mass spectral data. A modified liquid-liquid extraction scheme is now developed which provides this chemical information. The scheme separates complex mixtures into strong and weak acids, bases, polar and non-polar compounds, aldehydes and ketones. When GC/MS data is insufficient to settle identifications unambiguously, the chemical information associated with such fractions is decisive. Because the fractionation scheme greatly simplifies the analysis of complex mixtures, it is possible to identify and determine trace compounds in samples containing large amounts of other compounds, e.g. phenols, aldehydes, and ketones in diesel exhaust, suspected but not proven to be present.

160. LASERS IN ANALYTICAL CHEMISTRY 4.8 02-03
E. S. Yeung

This program is aimed towards the development of 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. Specific areas of concern include (1) the development of the laser microprobe for atomic spectroscopy on surfaces; (2) new optical detectors for liquid chromatography suitable for complex samples; (3) Raman methods and two-photon methods applied to analytical problems; (4) photoacoustic and interferometric concepts for improved absorption measurements; and (5) laser-induced chemiluminescence for specific gas analysis. Investigations include the fundamental principles behind the measurements, the evaluation of the analytical potentials, and the demonstration of the analytical method in representative samples.

Analysis

Chemistry Division
 Argonne National Laboratory
 9700 South Cass Avenue
 Argonne, Illinois 60439

Total \$300,000

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|---|-----|-------|
| 161. ANALYTICAL DEVELOPMENTS IN MASS
SPECTROMETRY-CHROMATOGRAPHY AND
SUPPORTING SYSTEMS
R. Hayatsu, R. E. Winans | 1.8 | 02-03 |
|---|-----|-------|

This program maintains up-to-date analytical methods and instrumentation necessary for the characterization of the maceral components of coals and the complex mixtures resulting from the partial oxidation or the liquefaction of coal. High-resolution and time-of-flight mass spectrometers (TOFMS) are used directly or in conjunction with high performance gas and liquid chromatography, and a computerized microwave plasma detector (MPD) is used to measure quantitatively, and simultaneously, the elements C, H, D, O, N, S, F and Cl. Direct TOFMS analysis of separated coal macerals has provided important information on the organic structures in these materials. Correlations of these results within individual coals and between macerals isolated from different coals are being made. A very sensitive coal elemental analyzer with direct oxygen determination is being developed using the MPD in conjunction with coal-fluorine chemistry. This program responds to the complex analytical problems which develop during coal chemistry studies.

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| 162. STUDY OF ATMOSPHERIC TRACE GASES BY
MASS SPECTROMETRY
C. M. Stevens | 1.5 | 02-03 |
|--|-----|-------|

A major aim of this program is the determination of the sources and production rates of atmospheric carbon monoxide and methane on a global scale by means of isotopic distribution measurements. The current technological component of the atmospheric CO in the northern hemisphere is being determined and compared to its global emission rate. The present concentration level is being compared to past levels, and the data is being used to infer long-term trends in hemispheric OH radical concentrations. The isotopic compositions of methane from natural sources are being determined and are used to estimate the isotopic inventory needed to account for the composition of atmospheric CH₄.

Analysis

Chemistry Department
 Brookhaven National Laboratory
 Upton, New York 11973

Total \$220,000

163. APPLICATIONS OF NUCLEAR METHODS TO ANALYSIS G. Harbottle, E. V. Sayre, R. W. Stoenner	2.3	02-03
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The basic thrust of this program is to extend and improve nuclear methods of elemental analysis, particularly methods such as neutron activation analysis that permit the determination of many components (including trace impurities) quickly and efficiently, and to develop methods 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, such as the dolomite strata enclosing commercial lead-zinc deposits, clays, other minerals and artifacts made from them. Studies of the accuracy and precision of standardization in activation analysis are an important part of the program. An improved proportional counter method for carbon-14 measurement in samples as small as 10 mg is being developed and applied to a number of problems.

Department of Energy and Environment, BNL, continued

166. DETERMINING FRAGILE MOLECULES IN THE ENVIRONMENT

1.7

02-03

Roger L. Tanner

The program goal is analytical methods development for trace amounts of potentially reactive constituents of environmental samples, emphasizing derivatization-chromatographic techniques which show promise in solving basic analytical problems involving by-products of energy-production technologies. Research is being conducted in the use of capillary-column GC with an electron capture detector for determination of polynuclear aromatic hydrocarbons (PAH) which may be nitratable (to form even more toxic by-products) by reaction with NO_2 or nitrite especially in the presence of oxidants in the atmosphere. Preliminary results of laboratory nitrations of PAHs indicate that use of reactivity scales and indexing schemes may permit the quantitative linking of parent PAHs and nitro-derivatives formed therefrom in the ambient atmosphere. A second area of focus is the use of liquid chromatography with post-column derivatization for trace determination of organic acids and phenols via cerium(IV) oxidation with fluorescence detection.

Analysis

Physics Department
 Brookhaven National Laboratory
 Upton, New York 11973

Total \$150,000

167. DEVELOPMENT AND APPLICATIONS OF
 NUCLEAR PARTICLE MICROSCOPY
 K. W. Jones and H. W. Kraner

1.9

02-03

The methods of nuclear and atomic physics are used to develop and apply techniques for the quantitative measurement and precise spatial localization of stable isotopes. Beams from a 3.5-MV Van de Graaff, MP Tandem Van de Graaff Facility, high flux reactor, and high intensity synchrotron x-ray source are used to identify isotopes through production of unique atomic and nuclear signatures. The use of proton and x-ray induced x-ray fluorescence, Rutherford backscattering, and nuclear reactions make possible the determination of multi-element concentrations with excellent sensitivity. Spatial distributions are determined by use of particle microbeams with a resolution of about 10 μm and depth distributions by nuclear reaction analysis or Rutherford backscattering with resolutions of .01 μm . Collaborative projects in a variety of disciplines are in progress and include in-vivo lead determinations, hydrogen profiling, and transport of heavy metals in graphite at high temperatures.

Analysis

Exxon Nuclear Idaho Co., Inc. Total \$50,000
Idaho National Engineering Laboratory
P. O. Box 2800
Idaho Falls, Idaho 83401

168. NEGATIVE SURFACE IONIZATION 1.0 02-03
MASS SPECTROMETRY
J.E. Delmore

This research is directed toward an improved understanding of the negative surface ionization (NSI) process for both elemental and molecular ions, and applications to isotopic analyses. NSI of Cl & I has been shown to have excellent potential for very wide ratio measurements of radioactive nuclides. The negative molecular ions from SF₆ have been shown to originate partly from NSI and partly from electron attachment. Overall ionization efficiency has been shown to be highly dependent upon the decomposition kinetics of the parent molecule on the hot ionizer. In turn, the kinetics are highly dependent upon the surface conditions of the ionizer. A major focus of the program will be to develop a more exact definition of this surface dependency. Another major focus will be the development of methods for overcoming the problems from the electron current generated from the hot filaments at negative potential. With improvements in the areas, other electronegative elements and molecules will be studied.

Analysis

Energy and Environment Division
 Lawrence Berkeley Laboratory
 University of California
 Berkeley, California 94720

Total \$100,000

169. CHEMICAL ANALYSIS

1.0

02-03

R. Giaque and R. Clem

The development and application of x-ray fluorescence (XRF) and anodic stripping voltammetry (ASV) trace chemical analysis methods is the fundamental basis of this program. Emphasis is placed on improving the sensitivity capabilities of these two techniques. The methods are applied to support (1) oil shale, (2) waste management, (3) atmospheric aerosol, and (4) geochemical research programs. A primary purpose of these programs is to study the distribution, speciation, and fate of numerous trace elements. Over forty elements can be determined using XRF methods. Typical sensitivities realized are 0.5 to 5 ppm using 20 to 30 minute analysis periods. ASV methods permit the determination of a number of reversibly electroreducible elements with typical sensitivities on the order of one part per billion or less.

Analysis

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total \$50,000

170. ANALYSIS OF TRANSPLUTONIUM ELEMENTS IN
DILUTE SOLUTION
S. D. Brown

0.5 02-03

The goal of this research is the development of rapid methods for analysis of metal species in aqueous samples, with emphasis on actinide species. Computer controlled electrochemical and spectroscopic methods are being developed for use with ion chromatographic separations of analyte from sample matrix. New approaches to data analysis of the electrochemical and spectroscopic data are being emphasized. A new method for separating overlapped electrochemical responses is being developed and tested. This method allows effective resolution of peaks and removal of noise; it will also be used in studies of complexation of trace metals in solution. Both thermodynamic and kinetic information related to metal complexation will be obtained by application of this technique to several laboratory systems. This information will allow the design of efficient separations, which will be used later in optimizing the chromatographic separations.

Analysis

Analytical Chemistry Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

Total \$1,100,000

171. ION MICROPROBE MASS ANALYSIS R&D: 1.4 02-03
SURFACE CHARACTERIZATION
W. H. Christie, R. J. Warmack,
R. E. Eby

The overall objectives of this program are: to develop state-of-the art methods for acquiring, processing, and quantifying SIMS data, and to develop methods for applying SIMS to the solution of surface analytical problems in on-going DOE research programs. Ion trajectory analysis work has led to the design and construction of modified ion optics that should correct for beam losses observed in a prototype cesium ion gun. These improvements will be tested during this period. SIMS is being used to study ion emission from U loaded resin beads on heated Re surfaces. This system is being studied in detail in order to unravel the mechanism of ionization. The dependence of ionization efficiency on the bead-filament interface will be given additional study. Ion implanted materials are being investigated as standards for quantifying sputtered ion yields. These materials are of special significance to SIMS as accurate standards can be prepared to calibrate the sputtering response in any chemical system.

172. ADVANCED SPECTROSCOPIC METHODS FOR 2.2 02-03
CHEMICAL ANALYSIS
L. Hulet, J. Dale, H. Dunn

The objective of this task is to develop advanced spectroscopic methodology and apply it to energy and environmental problems. New techniques under evaluation and development are: the production of monoenergetic positrons and their use for surface analysis and the characterization of condensed materials; the use of the Holifield Heavy Ion Facility as a tool for generating x-ray fluorescence and Auger electron spectra of solids and gases, and performing heavy ion lithography and tomography; the use of a miniature spectrometer for measuring electron spectra from microscopic objects. Principle areas of application of these methods are in nuclear energy technology and its associated problems, materials characterization, coal and its waste products, and trace element pollution.

Analytical Chemistry Division, ORNL, continued

173. MASS SPECTROMETRY R & D ORGANIC ANALYSES 2.4 02-03
W. T. Rainey, G. L. Glish,
E. H. McBay

This research is directed toward more efficient utilization of non-conventional mass spectrometric methods in analytical applications, especially those methods which are sensitive to molecular structure. The high resolution spectrometer is being used in various scanning modes to determine fragmentation patterns, appearance potentials, and kinetic energy release for various compounds. Construction of a triple sector spectrometer has led to emphasis on the use of mass spectrometry/mass spectrometry (MS/MS) for identification of gas phase ion structures, resulting in applications to direct mixture analysis. Types of MS/MS, unavailable to two sector instruments, are being explored. In addition, application of secondary ion mass spectrometry to involatile organic compounds is being investigated in conjunction with MS/MS. Initial studies using pyrolysis gas chromatography/mass spectrometry on representative coal samples have been completed. Hydrogen transport mechanisms are being studied by pyrolyzing specifically deuterated coals under various conditions to clarify aspects of the primary coal structure.

174. RESEARCH AND DEVELOPMENT OF ADVANCED 3.3 02-03
CHEMICAL MEASUREMENT TECHNIQUES
H. H. Ross, W. B. Whitten,
J. M. Ramsey, R. W. Shaw,
J. P. Young, L. N. Klatt

Various new spectroscopic techniques are being developed for enhanced analytical utility. One such technique, delayed lasing, was first demonstrated at ORNL last year. The method will be studied in detail to determine its potential applicability to absorption spectroscopy. New instrumentation concepts are being investigated for time-resolved fluorometric measurements. Novel analytical applications of fiber optic waveguides are being developed for time domain optical spectroscopy. Piezoelectric detection of optoacoustic signals is being applied to the selective and sensitive analysis of matrix-isolated organic materials. Laser excited optogalvanic spectroscopy is being tested for arsenic and fluorine analysis in a glow discharge detector. High resolution fluorescence excitation spectroscopy of molecular beams generated by laser ablation is being examined as a new solid sampling and analysis technique. Energy sources for these studies include conventional gas discharge lamps, gas and dye lasers, and heavy ions.

Analytical Chemistry Division, ORNL, continued

175. ORGANIC SECONDARY ION MASS SPECTROMETRY 0.6 02-03
P. J. Todd, W. H. Christie

This research is directed toward the development of the methodology of sputtering secondary ions from involatile organic sample targets. Exploratory experiments indicated that this ionization technique yields both molecular or pseudomolecular ions and fragments ions that are characteristic of the sample. Our initial efforts have been in constructing a secondary ion source with sufficient flexibility that factors such as primary ion chemistry, kinetic energy, intensity, and incidence angle can be evaluated with respect to sensitivity, secondary ion relative abundances and sample damage. The ion source constructed was designed with the aid of interactive computer ion optics programs, taking into account the known characteristics of secondary ion emission. It features oblique (70° from normal) primary ion incidence, high extraction potential, circular symmetry of the extraction and acceleration ion lenses, and two independent, orthogonal primary ion guns. The secondary ions emitted can be accelerated up to 10^4 volts to improve sensitivity and mass resolution.

176. MASS SPECTROMETRIC R & D FOR INORGANIC 2.0 02-03
AND ACTINIDE ANALYSIS
R. L. Walker, D. H. Smith,
T. R. Mueller

This work is directed toward improving analysis of samples of inorganic origin by thermal emission (TEMS) and spark source mass spectrometry (SSMS), toward devising new applications for these techniques, and toward improving the instrumentation involved. In TEMS a new ion source was designed and put into routine use. A layer of rhenium powder slurried with a sucrose solution resulted in enhanced ionization efficiency, reduction of fractionation, and improved precision. Application of resin bead loading will be extended to other elements, such as the rare earths. A turret source will be acquired and evaluated for its ability to yield analyses superior to present sample-changing arrangements. Initial exploration of laser ionization as an alternative to other techniques will be undertaken. In SSMS the beam chopper and automatic gap controller are in routine evaluation modes; further refinements to the technique will be developed and implemented.

Analysis

Physical Sciences Department
 Pacific Northwest Laboratory
 P. O. Box 999
 Richland, Washington 99352

Total \$625,000

177. ULTRASENSITIVE LASER-BASED SPECTROMETRIC ANALYTICAL TECHNIQUES
 R. C. Fukuda 1.0 02-03

The objective of this program is to develop ultrasensitive analytical techniques whose basis is laser-induced atomic and molecular spectroscopy. Currently, the photon burst and intracavity excited state absorption methods are being investigated. The photon burst method is based on the occurrence of resonant scatter of many photons by a single atom as it passes through a laser beam. Measurement of such time-correlated photons is being investigated as a method of isotopically specific single atom detection. Initial measurements are with cesium and its available isotopes. Design and construction of an intracavity excited state absorption spectrometer is being initiated. This device uses a pulsed dye laser to generate the excited states and cw intracavity absorption is used to detect them.

178. ANALYTICAL MASS SPECTROMETRY RESEARCH 2.7 02-03
 R. L. Gordon, C. R. Lagergren,
 D. M. Robertson, J. M. Kelley

This task addresses limitations on the application of mass spectrometry to analytical measurements which are due (1) to a lack of understanding of phenomena which are vital to effective measurements and (2) to limits imposed by existing instrumentation and techniques. The task is composed of three parts. The first seeks to elucidate mechanisms responsible for effective measurements by surface ionization mass spectrometry of subpicogram quantities of samples; the second explores new materials for surface ionization and new ionization techniques; the third is a continuing effort in the area of instrumentation development for mass spectrometry. Surface physical and chemical techniques are used to investigate the structure and composition of the surface ionization source, the dependence of the surface work function on bulk composition and temperature history, the kinetics of ion production, and the dependence of chemical pathways for ion production on sample loading techniques. Instrumentation development utilizes a mass spectrograph which has been assembled specifically for research on both sources and detectors for mass spectrometry.

Physical Sciences Department, PNL, continued

179. ULTRASENSITIVE RADIOACTIVITY SPECTRO- METRIC ANALYTICAL TECHNIQUES J. H. Kaye and F. P. Brauer	0.8	02-03
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The objective of this program is to develop new and improved ultrasensitive and selective radioactivity spectrometric techniques for analysis of radio-nuclides. The concept of time-of-event counting, wherein the time at which each decay event occurs as well as its pulse height are recorded, is being evaluated to determine whether lower detection limits and better precision can be obtained as compared with conventional counting methods. Methods for reducing the background and improving the sensitivity of radiation detectors are being developed. These include use of phoswich detectors for beta-gamma coincidence counting, fabrication of special detectors for measuring radioactivity in gases, on-line computer analysis of individual pulses from radiation detectors, and exploitation of unique and specific correlations between decay emissions. A counting facility is being set up in a tunnel in Gable Mountain which will provide massive shielding from cosmic radiation for low-background counting experiments.

180. COMBINED ATOMIC ABSORPTION-MASS SPEC- TROMETRIC ANALYTICAL TECHNIQUES D. L. Styrís and J. H. Kaye	0.8	02-03
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The purpose of this program is to determine the mechanisms responsible for the high temperature analyte-matrix-furnace interactions which are important to the precision and sensitivity of furnace atomic absorption spectrometric analyses. A unique combination of furnace atomic absorption and mass spectrometric techniques is being used to simultaneously monitor the neutral atoms, ions and molecular species that are emitted when selected matrices are brought to elevated temperatures within particular metal or graphite furnaces. The results of these emission studies are used to identify and characterize the controlling chemical and physical processes. The systems being studied currently are vanadium, rubidium, silver and arsenic in both vitreous carbon and tantalum furnaces.

Analysis

Laser Research and Development Department
Sandia National Laboratories/Albuquerque
P. O. Box 5800
Albuquerque, New Mexico 87115

Total \$50,000

181. MASS SPECTROMETRY WITH LASER IONIZATION	0.6	02-03
A. Wayne Johnson and A. V. Smith		

The purpose of this research is to develop methods of increasing the sensitivity and selectivity of mass spectrometers by using light from tunable dye lasers as the source of ionization via multiphoton ionization. Molecules are preselected before entering the mass selector by tuning the lasers to intermediate resonances. This is useful in separating molecules of nearly equal masses and in separation of isomers which is virtually impossible today with mass spectrometers. Quadrupole and time-of-flight mass spectrometers are compared to determine the advantages of each, although initial results are indicating that the time-of-flight is particularly suited to use with pulsed (< 10 nsec) lasers. A substantial increase in mass resolution is demonstrated in a time-of-flight instrument using a 5 ns light pulse rather than the conventional e-beam pulse.

Chemical Engineering Sciences

Nuclear Energy Department
Brookhaven National Laboratory
Upton, New York 11973

Total \$75,000

182. TWO PHASE FLOW STUDIES
N. K. Tutu

1.0

02-04

This investigation is directed towards the goal of developing a simple, low cost, and objective method of flow pattern recognition in two phase gas-liquid flows. Since pressure fluctuations provide the basis for the present detection scheme, this technique is applicable to arbitrarily large sized ducts without increasing the cost or complexity. Software for high speed data acquisition and statistical signal analysis is being developed. Measurements are being made during the bubbly, slug, churn-turbulent, and annular flow regimes; and include the probability density function, power spectral density, auto-correlation, and cross-correlation. These basic experimental data are also expected to be valuable to researchers developing theoretical models for the prediction of vapor growth in two phase bubbly flows.

Chemical Engineering Sciences

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total \$210,000

183. TURBULENT COMBUSTION

2.5

02-04

F. Robben, R. K. Cheng
and L. Talbot

The interaction of fluid mechanical turbulence with combustion is being studied experimentally for premixed fuel/air conditions. Laser Rayleigh scattering and laser Doppler velocimetry are used to provide spatially and temporally resolved measurements of density and velocity; these parameters are sufficient to characterize the relevant features of turbulent premixed combustion. Two idealized flow configurations are developed, 1) the turbulent boundary layer over a strongly heated wall where lean combustion occurs, 2) an unconfined V-shaped premixed turbulent flame. The flowfield of the heated turbulent boundary layer has been analyzed in detail as the necessary prerequisite for studying the cases involving combustion. The results of the flame study have demonstrated the importance of the geometry of the fluctuating flame in influencing turbulence statistics throughout the flowfield.

Chemical Engineering Sciences

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Total \$90,000

184. HIGH-PRESSURE EQUILIBRIA IN HYDROCARBON-
WATER (BRINE) SYSTEMS 1.3 02-04
J. M. Prausnitz

The goal of this project is to obtain quantitative understanding of phase behavior in deep aquifer deposits wherein natural gas (mostly methane) is in equilibrium with water (or brine) at high pressures (1-2 kilobars). Toward that end, a high-pressure equilibrium cell has been constructed for the region ambient to 350°C. The apparatus is now in the final testing stage. Samples of the vapor and the liquid are analyzed by chromatography and, for salt, by titration. A molecular model of the Van der Waals' form has been constructed to interpret and correlate high-pressure, vapor-liquid equilibrium data for water-gas systems, toward facilitating engineering-design calculations. A two-fluid model is used to allow for nonrandom mixing. To reduce the model to practice, special computer programs are under development that assure convergence of trial-and-error calculations at all fluid densities, including the critical region. Apparatus has been constructed toward equilibrium (solubility) measurements for high-pressure (supercritical) extraction.

Chemical Engineering Sciences

Chemical Technology Division
 Oak Ridge National Laboratory
 P. O. Box X
 Oak Ridge, Tennessee 37830

Total \$75,000

185. FUNDAMENTAL PROCESSES IN SORPTION PUMPING AND TRANSFER OPERATIONS USING DEEP BEDS OF SORBENTS P. W. Fisher	0.7	02-04
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Processes involving pumping, storage, and transfer of materials by sorption on deep beds of sorbents are being utilized in several energy production and energy storage areas. These techniques, once limited to laboratory-scale operations, are being proposed for large-scale applications. This research seeks a fundamental understanding and analysis of the chemical engineering of these operations. Deep-bed sorption processes are studied experimentally to determine the relative importance of heat transfer, mass transfer, pressure drop, equilibrium, and reaction kinetics. Physical properties such as thermal conductivities, diffusivities, equilibrium adsorption isotherms, and reaction rate constants are either derived from the literature or determined in separate experiments. The data are used to study mathematical modeling techniques to predict the performance of deep-bed sorption systems.

Chemical Engineering Sciences

Chemical Technology Department
Pacific Northwest Laboratory
P. O. Box 999
Richland, Washington 99352

Total \$75,000

186. DEVELOPMENT OF PREDICTIVE MODELS FOR FLUIDIZED BEDS AND ENTRAINED SUSPENSIONS USED IN COAL CONVERSION PROCESS C. T. Li	1.0	02-04
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The purpose of this project is to develop mathematical models which allow reliable design and evaluation of fluidized bed and entrained suspension systems used in coal conversion processes. Models developed are expected to predict the performance of fluidized beds as a function of system size and configuration, chemical reactions, and physical changes occurring with various coal conversion reactor systems. Specific tasks are: (1) finishing a study of gas jetting phenomena at the distributor zone of a fluidized bed, (2) developing a two-phase/two-zone model and testing the validity of this model, and (3) incorporating the elutriation zone model into the two-phase/two-zone model for incorporation into a more generalized two-phase/three-zone model.

Chemical Engineering Sciences

Combustion Sciences Department
Sandia National Laboratories/Livermore
Livermore, California 94550

Total \$150,000

187. ANALYSIS OF REACTING, TURBULENT FLOWS
B.R. Sanders, W. T. Ashurst

1.5

02-04

This research consists of the development and application of an unsteady, turbulence computational procedure to the practical combustion situation of high Reynolds number and large heat release. The fluid mechanics of turbulent mixing is computed by a discrete vortex transport technique, known as Vortex Dynamics. To date this procedure has been limited to incompressible flows, and for most applications to two spatial dimensions. The tasks of this project consist of incorporating the transport of a conserved scalar, such as the relative concentration of a fuel and oxidizer; incorporation of the third spatial dimension; and to include the effects of variable density for large heat-release systems. The main focus of this research is in analyzing turbulent reacting jets for which experimental data is available through a complimentary BES program at the Sandia Combustion Research Facility.

Photochemical and Radiation Sciences

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

188. STUDY OF THE MOTION OF ELECTRONS IN NON- POLAR CLASSICAL LIQUIDS \$60,000 01-01
G. Ascarelli
Department of Physics

This research is designed to help understand the details of the motion of electrons in non polar classical liquids. The Hall mobility is a traditional measurement to identify scattering mechanisms of electrons in solids; we expect that it will contribute in liquids as well. We use the Redfield technique for Hall measurements. It uses blocking electrodes and pulsed electron currents. The liquid under study is tetramethyl silane. Our preliminary room temperature results indicate a Hall mobility of $100\text{cm}^2/\text{Vs}$ that is about 10% larger than the traditional time-of-flight mobility measured on the same sample. If this difference will be confirmed by more accurate measurements extended over a wider temperature range we expect to be able to identify the possible scattering mechanisms. Work associated with preparation of the f.i.r. experiment is continuing.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

189. STUDIES IN CHEMICAL REACTIVITY \$65,965 01-01
Robert W. Carr, Jr.
Department of Chemical Engineering
and Materials Science

An investigation of the 313 nm photooxidation of 1,3-dichlorotetrafluoroacetone has been completed, and a mechanism consistent with observed reaction product yields has been deduced. An investigation of the flash photolysis of ketene, using time resolved mass spectrometry to detect intermediates and products, and also to follow the time dependence of the species concentrations, is being carried out. Emphasis is being placed upon the reactions of $\text{CH}_2(^3\text{B}_1)$. A re-design of this apparatus has been accomplished, and construction of components completed. Assembly will commence upon completion of the ketene work. The modifications will permit a 10^3 gain in detection sensitivity. An apparatus for highly sensitive detection of laser excited luminescence has been built. A flashlamp-pumped dye laser is used to photodissociate diazomethane at photon energies sufficient to produce $\text{CH}_2(^1\text{B}_1)$. Luminescence [$\text{CH}_2(^1\text{B}_1) \rightarrow \text{CH}_2(^1\text{A}_1)$] is detected as a function of excitation wavelength and pressure of added quenchers.

Photochemical and Radiation Sciences, continued

BOSTON UNIVERSITY
Boston, Massachusetts 02215

190. INVESTIGATIONS OF THE TRIPLET STATES OF CHLOROPHYLLS	\$163,000 24 mo. FY81-82	01-01
Richard H. Clarke 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 (non-destructive) probe into the makeup of photosynthetic systems. Our research program utilizes optical detection of magnetic resonance spectroscopy to investigate the triplet state properties of the isolated molecule and solutions of aggregated chlorophylls. These measurements allow an evaluation of in vitro chlorophyll systems for structural features proposed as models for the antenna and reaction center of photosynthetic systems in vivo and for their general applicability as model systems for photosynthesis.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

191. SENSITIZATION AND QUENCHING IN THE CONVERSION OF LIGHT ENERGY INTO CHEMICAL ENERGY	\$105,000 24 mo. FY81-82	01-01
Stanley J. Cristol Department of Chemistry		

The long-range objectives of this project are to learn how to define the factors, both qualitative and quantitative, which affect the quantum yields and chemical yields of sensitized and the analogous unsensitized reactions. Photosensitization and its obverse, quenching, are being studied in a variety of photochemical reactions, with attention paid to the sources of inefficiency (energy wastage) in such processes. Fundamental data on reaction-rate constants and excitation-transfer rate constants for photoisomerization and other reactions are being measured by several complementary techniques. Preliminary experiments on the geometric requirements for excitation and/or electron transfer are being conducted, as are possibilities for correlations between structure and excited-state reactivities.

Photochemical and Radiation Sciences, continued

THE OHIO STATE UNIVERSITY
Columbus, Ohio 43210

192. PULSE RADIOLYSIS STUDIES OF FAST REACTIONS IN MOLECULAR SYSTEMS Leon M. Dorfman Department of Chemistry	\$153,786 24 mo. FY 81-82	01-01
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The central objective of this project is the determination of the rates and mechanisms of chemical reactions induced by high energy radiation. This is being done by using the fast reaction technique of electron pulse radiolysis in the direct observation of short-lived intermediates by fast optical detection (time resolution 5 nanoseconds). The optical absorption spectra of the reactive transients, which determine the course of the chemistry, are also being obtained. Current activities focus on two areas: (a) the reactivities of organic molecular ionic species (carbocations and carbanions) in solution. These ionic species play a role in catalytic reactions of hydrocarbons and in the initiation of cationic polymerization. (b) the reactivities and optical absorption spectra of transition metal carbonyl radicals, specifically $MN(CO)_5^{\bullet}$ and $Re(CO)_5^{\bullet}$. The reactivities of this type of free radical are relevant to homogeneous catalysis. Since the reactions under investigation are initiated by high energy electrons, the results of all of the foregoing relate to radiation chemical systems.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

193. TIME-RESOLVED RESONANCE RAMAN AND ENERGY TRANSFER STUDIES ON BACTERIORHODOPSIN AND OTHER PHOTOCHEMICAL SYSTEMS M. A. El-Sayed Department of Chemistry	\$77,366	01-01
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The objective of this study is to understand the mechanism by which the simplest naturally occurring photosynthetic bacteriorhodopsin (bR) system stores solar energy. Our emphasis is to study the primary processes, the absorption act and the formation of the photochemically and thermally formed transients in the millisecond to picosecond time scale. Time resolved resonance Raman techniques have been developed to examine the vibration spectra of the chromophore (retinal) and to obtain structural information on these transients. Time resolved protein fluorescence techniques have also been developed to follow the changes in the protein as a result of the photosynthetic act. Time resolved polarized-photochemical techniques are being developed for detecting energy migration processes prior to the photochemical change in this system.

Photochemical and Radiation Sciences, continued

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

194. PHOTOCHEMICAL ACTIVATION AND REACTIVITY OF POLYNUCLEAR TRANSITION METAL COMPLEX MOLECULES \$90,000 01-01
John F. Endicott and Richard L. Lintvedt
Department of Chemistry

This research program is directed towards the generation of molecular complexes capable of photoinduced, multielectron transfer. To this end new series of bi-nuclear and tri-nuclear, bis-triketone and bis-tetraketone respectively, complexes are being synthesized and characterized. A significant part of the characterization involves electrochemical studies of thermal multielectron capabilities of metals in these coordination environments. Most of the thermal studies have centered on the sequential two electron reductions of $[\text{Cu}^{\text{II}}, \text{Cu}^{\text{II}}]$ and $[\text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}]$ complexes. Exploratory photophysical studies of mixed metal- UO_2 complexes are being pursued with a view of generating metastable, charge separated species (e.g., $[\text{UO}_2^{2+}, \text{Ni}^{\text{II}}] \xrightarrow{h\nu} [\text{U}^{\text{V}}, \text{Ni}^{\text{III}}]$) which can be utilized in oxidation of molecular substrates. Fundamental photophysical studies involving intramolecular energy and electron-transfer in both binuclear and trinuclear mixed metal complexes are being carried out by intramolecular quenching measurements, excited-state life-time measurements, etc.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

195. PHOTOCHEMICAL SOLAR ENERGY CONVERSION IN SURFACTANT VESICLES \$55,000 01-01
Janos H. Fendler
Department of Chemistry

The objective of this program continues to be the utilization of surfactant vesicles in photochemical solar energy conversion and hydrogen generation. Advantage has been taken of potential gradients available in charged surfactant vesicles to induce charge separation, energy and electron transfers and hydrogen production. Photosensitized electron transfer from tris(2,2'-bipyridine)ruthenium cation, $\text{Ru}(\text{bpy})_3^{2+}$, to methylviologen, MV^{2+} , in the presence of negatively charged dihexadecylphosphate, DHP, represents the most promising system. $\text{Ru}(\text{bpy})_3^{2+}$ was attached to the outer and MV^{2+} was placed onto the inner surfaces of DHP vesicles. Electron transfer from excited $\text{Ru}(\text{bpy})_3^{2+}$ to MV^{2+} across the bilayers of vesicles in the presence of externally added EDTA resulted in the formation of reduced methylviologen, $\text{MV}^{\cdot+}$, up to 75% conversion with a quantum efficiency of 10^{-2} . If additionally, 10^{-7} M PtO_2 was entrapped in the interiors of DHP vesicles, $\text{MV}^{\cdot+}$ promptly reformed with concomitant hydrogen evolution. Photolysis of this system leads to the net consumption of only EDTA at very low stoichiometric $\text{Ru}(\text{bpy})_3^{2+}$, MV^{2+} , and PtO_2 concentrations. Polymerizable surfactant vesicles capable of greater efficiency and stability are being developed.

Photochemical and Radiation Sciences, continued

THE OHIO STATE UNIVERSITY
Columbus, Ohio 43210

196. KINETICS OF FAST REACTIONS OF EXCITED SPECIES \$60,581 01-01
Richard F. Firestone
Department of Chemistry

Goals include elucidation of mechanisms for growth and decay of excited rare gas atoms and rare gas excimers in rare gases and in mixtures with molecular quenching agents subjected to a pulsed relativistic electron beam. Identities and relative contributions of excited atom precursors of bound singlet and triplet excimer states are sought via analysis of effects of T, P and quenching agents on the temporal behavior of excited species. Monitoring of excited species is performed via emission spectrometry and fast absorption spectrophotometry using tunable cw dye laser probing beams and fast detectors. The catalytic role of N₂ in conversion of Ar(1s) atoms to triplet excimers by interaction of N₂(C) with Ar₂ van der Waals molecules is also under investigation by means of continuum source spectrophotometric monitoring of triplet excimers coupled with pulsed N₂ laser induced perturbation of the N₂(C) population.

COLUMBIA UNIVERSITY
New York, New York 10027

197. LASER ENHANCED CHEMICAL REACTION STUDIES \$125,900 01-01
George W. Flynn 24 mo.
Department of Chemistry FY80-81

This research project consists of a series of experiments which are designed to probe the photochemical effects of laser radiation with particular emphasis on the role of energy transfer in reactive processes. Infrared laser excitation of sulfur hexafluoride, methyl fluoride, and perfluorocyclobutane are being studied with a low power, continuous wave carbon dioxide laser in a supersonic molecular beam apparatus. Collisions are used to enhance the level of excitation which can be achieved via laser pumping. The reactivity of vibrationally excited molecules is being studied in the same apparatus. In a separate experiment molecules are being photofragmented with a high power, pulsed excimer laser. High velocity fragments produced in this way are being used to study the vibrational excitation and chemical reactivity of molecules. Photochemical experiments are being performed on bromine molecules trapped in a rare gas matrix at 10°K. The dynamics of photodissociation of bromine in a solid cage are altered from those in the gas phase.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF TEXAS
Austin, Texas 78712

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| 198. SOLAR-INDUCED ORGANIC PHOTOCHEMISTRY AT
SEMICONDUCTOR SURFACES
Marye Anne Fox
Department of Chemistry | \$99,100
24 mo.
FY80-81 | 01-01 |
|---|-------------------------------|-------|

A series of chemically-modified semiconductor photoanodes are being prepared. Such electrodes are more efficient in photogalvanic operation than are their unmodified counterparts. Carbanions and oxocarbon derivatives are being tested as sensitizers for photoelectrochemical cells. Oxidative and reductive coupling reactions of several carbanions are being examined to determine whether these occur by initial photoinduced single electron transfer. A new redox photochromic system (a pentacyclic nitrogen-containing quinone) has been discovered and its photochemical mechanism is being elaborated.

WASHINGTON UNIVERSITY
St. Louis, Missouri 63130

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| 199. REACTION STUDIES OF HOT SILICON AND
GERMANIUM RADICALS
Peter P. Gaspar
Department of Chemistry | \$80,500
14 mo. | 01-01 |
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The goals of this research program are to discover what are the reactions of high energy Si and Ge atoms, how do the reactions take place, and what are the relationships among structure, energy, and reactivity that determine the products formed. The reactions of recoiling silicon and germanium atoms from $^{31}\text{P}(n,p)^{31}\text{Si}$, $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$, $^{76}\text{Ge}(n,2n)^{75}\text{Ge}$, and $^{74}\text{Ge}(n,\gamma)^{75}\text{Ge}$ with simple inorganic and organic substrates are being investigated and the chemically stable end products identified. Reaction mechanisms are elucidated by studying the variation in product yields with changes in reaction parameters, and by comparison of products from recoil reactions with those formed from chemically generated atoms, ions and radicals. In the past year new evidence has been found for both neutral and ionic pathways for ^{31}Si .

Photochemical and Radiation Sciences, continued

TEMPLE UNIVERSITY
Philadelphia, Pennsylvania 19122

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| 200. DYNAMIC ASPECTS OF THE DYE-SENSITIZED
PHOTOCONDUCTIVITY OF SEMICONDUCTORS
Antonio M. P. Goncalves
Department of Chemistry | \$130,000
24 mo.
FY 81-82 | 01-01 |
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This research program is designed to probe the dynamics of the elementary processes (injection, recombination, and escape) which determine the efficiency of dye-sensitized semiconductor/electrolyte solar cells. The general experimental approach relies on the use of ultrafast excitation and time-resolved detection techniques. Injection rate constants are being explored by measurement of the fluorescence lifetime of dyes adsorbed on semiconductors. The experimental arrangement uses pulses from a Nd:glass laser system and detection by a streak camera, with an overall time resolution roughly 2 picoseconds. Processes which follow injection and destroy the oxidized dye are being characterized by time-resolved transient absorption experiments which use a dual beam laser instrument with a 175 ps time resolution. A systematic study of the various processes is being made with a series of dyes of varying excited state energies, both above and below the conduction band of the semiconductor.

UNIVERSITY OF FLORIDA
Gainesville, Florida 32611

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| 201. RADIATION CHEMISTRY OF HYDROCARBON AND
ALKYL HALIDE SYSTEMS
Robert J. Hanrahan
Department of Chemistry | \$56,000 | 01-01 |
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Work at the University of Florida is directed towards understanding of the primary and secondary chemical processes which lead to formation of net products in the gamma or pulsed electron radiolysis of simple chemical systems. A study of the radiolysis of H₂-CO mixtures has revealed formation of numerous hydrocarbon and oxygen-containing products both in unpacked vessels and in vessels packed with finely divided alumina or other active surfaces. Recent measurements have dealt with effects of temperature and pressure in this system. Studies on the pulsed electron radiolysis of CF₃I and CH₃I have developed rate constants for loss of ²P_{1/2} and ²P_{3/2} atomic iodine, as measured at 206 and 178 nm. Experiments on high pressure mass spectrometry and photochemistry of CF₃I-CH₃I mixture have provided, respectively, information concerning ionic and free-radical reaction pathways in the radiolysis of this system. Measurements are being made on hydrocarbon product yields from radiolysis of pure gas phase propane, in preparation for an investigation of radiation induced oxidation in this system.

Photochemical and Radiation Sciences, continued

BOSTON UNIVERSITY
Boston, Massachusetts 02215

202. STUDY OF INTERMEDIATES FROM TRANSITION METAL EXCITED-STATE ELECTRON-TRANSFER REACTIONS	\$125,088 24 mo. FY81-82	01-01
Morton Z. Hoffman Department of Chemistry		

A study is being undertaken to investigate the kinetic and mechanistic behavior of one-electron reduced polypyridyl (and related) complexes of transition metals in aqueous solution. These species are being generated from the reductive quenching of the excited states of the parent complexes using conventional and laser flash photolysis techniques, or from the interaction of the parent complexes with radiation-generated reducing radicals using continuous and pulse radiolysis techniques. We are investigating the dependence of the rates and stoichiometries of the reactions of the one-electron reduced species on the nature of solution medium, the presence or absence of catalysts, and the application of activation conditions. Particular emphasis is being placed on understanding the relationships among the structure of the ligands, the nature of the metal center, and the kinetic parameters of their substitution and redox reactions.

FLORIDA STATE UNIVERSITY
Tallahassee, Florida 32306

203. RADIATION INDUCED REACTIONS IN ORGANIC SYSTEMS	\$42,000	01-01
Russell H. Johnsen Department of Chemistry		

This research is concerned with the fundamental processes which follow the absorption of high energy radiation and the reactions of the transient intermediates generated by this energy absorption. Presently the work is focussed on two areas: the production and reactions of free radicals, especially radical pairs in molecular crystals, and the kinetics of reaction of gas-phase hydroxyl radicals. Radical pairs appear to be the chief stable products produced during the low temperature irradiation of aromatic azoxy compounds. The kinetics of recombination of these species and their relation to the previously studied isolated radicals are unexpectedly complicated. The rate constants, activation energies and traps involved will be investigated using esr spectroscopy. The reactions of hydroxyl radicals with a variety of aromatic compounds is under investigation utilizing a continuously mass-analyzed flow system with photochemically generated radicals. The mechanisms of production of a variety of hydroxylated and condensed products are under investigation.

Photochemical and Radiation Sciences, continued

BOSTON UNIVERSITY
Boston, Massachusetts 02215

204. ORGANIC PHOTOCHEMICAL STORAGE OF SOLAR ENERGY \$80,000 01-01
Guilford Jones, II
Department of Chemistry

Mechanisms of photosensitization suitable for driving isomerization of organic compounds are under investigation. Isomerization reactions include those capable of storing radiant energy as latent heat in kinetically stable molecules. Sensitizing or complexing agents of the electron transfer or energy transfer type are employed for the activation of isomerizable substrates. Sensitization mechanisms involve several important classes of photochemical reaction intermediates, including exciplexes, radical-ions, and excited triplet states. The mechanisms of photosensitization are studied using the techniques of emission spectroscopy, flash photolysis, magnetic polarization (CIDNP), and quantum yield determination. Recent emphasis is placed on the photochemistry of charge-transfer complexes and on the temperature dependence of electron and energy transfer processes which are important for isomerization and other reactions.

UNIVERSITY OF ILLINOIS
Urbana, Illinois 61801

205. EXCITED STATE ELECTRON TRANSFER IN SYSTEMS WITH A WELL-DEFINED GEOMETRY \$25,100 01-01
K. J. Kaufmann
Department of Chemistry

Solar energy conversion in green plants and photosynthetic bacteria is extremely efficient. Consequently we have chosen to study two systems that may mimic some of the early steps in photosynthesis. The first system is a cyclophane containing a chlorophyll and a pheophytin macrocycle. The second complex consists of a porphyrin and a quinone joined with two covalent linkages. The light activated electron transfer is being followed in two ways. The decay of the singlet excited state is monitored via fluorescence, while the buildup of a radical pair is observed using time resolved absorption spectroscopy. The structure of these complexes can be varied by changing solvent and by adding ligands such as pyridine. Circular dichroism, infrared absorption spectroscopy, nmr and esr are being used to characterize these changes in structure. The influence of structure and the effect of temperature on the rate of electron transfer are being used to test various theories of electron transfer.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

206. PHOTOELECTROCHEMISTRY AT IRON OXIDE
ELECTRODES \$48,000 01-01
John H. Kennedy
Department of Chemistry

The object of the research program is to extend the knowledge of semiconductor photoelectrochemistry for the decomposition of water into hydrogen fuel and oxygen. In particular, a study of iron oxide electrodes in various electrolytes is being investigated. Semiconductor n-Fe₂O₃ is produced by chemical doping, especially with the addition of group IV elements such as Si, Ge, and Ti. Iron oxide doped with Cr₂O₃ is also under investigation because chromium oxide has a lower bandgap than iron oxide and may, therefore, extend the photoresponse to longer wavelength. Spectral sensitivity, photocurrent efficiency, and chemical products produced at these various doped iron oxide materials are studied. Competition between solute species for photogenerated electron holes at the electrode surface is a major objective of the program. Competition between halide and hydroxide ions has been studied and is being extended to various organic solutes.

LOUISIANA STATE UNIVERSITY
Baton Rouge, Louisiana 70803

207. THEORETICAL STUDIES OF EXCESS ELECTRONS \$39,218 01-01
IN FLUIDS: STRUCTURE AND ELECTRON
TRANSFER
Neil R. Kestner
Department of Chemistry

This research involves the calculation and predictions of the properties of trapped electrons in various polar media. We are exploring the stability of small clusters of polar molecules surrounding an electron. We are also calculating other properties of these systems which can be experimentally determined. In addition a major portion of the research concerns the electron transfer process involving these trapped electrons and electron transfer reactions in polar media in general. We are particularly concerned with the rate of highly exothermic processes and with the temperature dependence of such reactions. We already have results which indicate that these reactions have very unusual temperature dependences.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF HOUSTON
Houston, Texas 77004

208. CHARGE SEPARATION IN PHOTOREDOX REACTIONS	\$90,000	01-01
Larry Kevan	16 mo.	
Department of Chemistry	FY80-81	

The objective of this research is to probe the molecular mechanistic and structural aspects of charge separation in photoredox reactions in micellar 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 and cationic surfactants. The cation is observed by electron spin resonance and electron spin echo (ESE) spectrometry. ESE modulation analysis is being used to detect very weak hyperfine interactions so as to locate where the cation is in the micelle and to measure the cation interaction with the water phase surrounding the micelle. Effects of micelle size are being detected and analyzed. The effects of electron scavengers both within the micelle and at the polar surface of the micelle are also being studied by ESE methods in order to locate the electron relative to the cation. Metal ion scavengers in bulk solution and at the micelle surface can be distinguished by ESE.

THE UNIVERSITY OF ALABAMA
Tuscaloosa, Alabama 35486

209. ELDOR INVESTIGATIONS OF RADIATION PROCESSES	\$52,526	01-01
Lowell D. Kispert		
Department of Chemistry		

The goal of this research is to determine how a crystalline lattice affects energy transfer and primary radiation and photochemical processes in irradiated organic crystals. Such information is vital to understanding photo-induced solid-state polymerization and stereospecific reactions in solids. Electron spin resonance, electron-nuclear double resonance and electron-electron double resonance spectroscopy are being used to identify the molecular fragments formed and to detect the energy transfer processes that occur. In particular, selected model low molecular weight halogenated carboxylic acid and acetamide crystals are being studied to determine the effect of hydrogen bonding on radical formation and stability as a function of temperature in crystals containing a) varying number of waters of crystallization, b) rotational disorder, c) chirality, d) impurities, and e) varying crystallographic forms. Electron attachment and oxidation processes for model systems containing chlorine and bromine as substituents are being determined as a function of reaction coordinate and excitation source.

Photochemical and Radiation Sciences, continued

THE JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

210. STUDIES IN HOT ATOM AND RADIATION CHEMISTRY \$75,997 01-01
Walter S. Koski
Department of Chemistry

In this investigation ion-beam techniques are being used to elucidate the ionic mechanisms of hot atom processes associated with nuclear transformations. Emphasis is being placed on the bromine-ethane system because of the extensive amount of work that has been carried out in this area. These published studies, however, are incomplete since they fail to account for the thermal ionic yield of CH_3Br as a function of moderator (Kr) pressure. Examination of all possible Br^+ ionic reactions with ethane shows that no direct reactions between these reactants account for the thermal ionic yield of CH_3Br . Studies of the collisions between Br^+ and Kr show that the Kr is not "inert" but participates in an active chemical way in the overall hot atom mechanism. Ions such as BrKr^+ , BrKr_n^+ and CH_3BrKr^+ are formed. Bond energies and heats of formation of BrKr^+ and CH_3BrKr^+ are being determined. Excited states of these ions can react with C_2H_6 and produce CH_3Br and they account for the pressure dependence of the yield on Kr. Such considerations are applicable to other hot atom systems where ions are involved.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

211. STUDIES IN CHEMICAL DYNAMICS \$80,000 01-01
Aron Kuppermann
Department of Chemistry

The goal of this research is to develop information about the energetics of excited states of molecules and ions and to investigate reactive and non-reactive molecular collisions. Low-energy electron scattering spectroscopy is used to measure the excitation energies of spin-forbidden and spin-allowed electronic transitions of families of organic and inorganic molecules. Pulsed photoacoustic and multiphoton ionization ultraviolet laser spectroscopy are used to study spin-forbidden transitions in some molecules at optical resolution. Variable angle photoelectron spectroscopy is used to identify the nature of the molecular orbitals from which electrons are photoejected by vacuum-ultraviolet radiation. Experiments in crossed molecular beams are used to determine intermolecular forces and to study reactive processes.

Photochemical and Radiation Sciences, continued

THE PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

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| 212. | THE PHOTOCHEMISTRY AND RADIATION CHEMISTRY OF VOLATILE SILANES, GERMANES AND PHOSPHINES
F. W. Lampe
Department of Chemistry | \$88,381 | 01-01 |
|------|---|----------|-------|

This research program is comprised of studies of the elementary chemical reactions and reaction mechanisms brought about by the irradiation of gaseous silanes, germanes and phosphines with ionizing radiation, infrared radiation and vacuum-ultraviolet light. The photodecompositions are being investigated using continuous irradiation by vacuum-ultraviolet radiation of 147.0 nanometers and pulsed infrared radiation of 9000-11,000 nanometers from a CO₂ TEA laser. Ionic species, SiH_x⁺, GeH_x⁺ and PH_x⁺ produced by an electric discharge, are reacted in the gas phase with neutral molecules such as the parent silane, germane, or phosphine, and other substances, and the lifetimes and collisional stabilization dynamics of energy-rich collision complexes, through which many of the reactions proceed, are examined in detail. Other ion-molecule reactions under study include CH₃⁻ and C₂H₅⁻ ion abstractions from alkyl silanes, and the reactions characteristic of SiF₄-H₂ and SiF₄-SiH₄ mixtures.

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

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| 213. | CRITICAL COMPILATIONS OF PHYSICAL AND CHEMICAL DATA
D. R. Lide, Jr.
Office of Standard Reference Data | \$118,000
\$ 82,000 | 01-01
02-01 |
|------|---|------------------------|----------------|

This program is designed to provide evaluated data compilations and critical reviews in areas of chemistry and physics relevant to DOE research and development programs. Projects active in FY 1981 cover the following subjects: 1) equation of state and thermodynamic properties of air and its constituents; 2) thermodynamic properties of ethylene; 3) X-ray production cross sections through K-shell ionization by H⁺ and He⁺⁺ for elements helium to uranium; 4) chemical kinetic data for reactions of metastable electronically excited species; 5) aqueous solubility and related parameters for selected compounds derived from coal, and 6) atomic transition probability data pertinent to controlled fusion research. Each of these projects is expected to lead to a published review giving recommended values for the properties in question. The program is administered by the Office of Standard Reference Data of the National Bureau of Standards, and additional projects of the same nature are supported by NSF, ONR, and NBS.

Photochemical and Radiation Sciences, continued

BRANDEIS UNIVERSITY
Waltham, Massachusetts 02254

214. PHOTOCHEMICAL REACTIONS OF COMPLEX MOLECULES IN CONDENSED PHASE \$80,000 01-01
Henry Linschitz
Department of Chemistry

Charge transfer interactions of excited molecules with appropriate donors or acceptors may lead either to thermal dissipation (quenching) or formation of primary free radicals which store the excitation energy in chemical form. The factors controlling the partitioning of excitation energy between these two competing pathways are being studied in this program. The two main classes of compounds used as test systems are metalloporphyrins in photooxidation reactions and ketones in photoreduction. The extent of primary radical formation is followed in both cases by means of laser flash photolysis. Comparison between energy-storing efficiency of reactions from singlet vs. triplet excited states is made by measuring relative radical yields as function of donor or acceptor concentration. Other variables being investigated are excited state redox potential, solvent polarity and viscosity and effects of proton shifts which are associated with the primary electron-transfer.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

215. THE CONTRIBUTION OF ELECTRONICALLY EXCITED STATES TO THE RADIATION CHEMISTRY OF ORGANIC SYSTEMS \$130,000 01-01
18 mo.
Sanford Lipsky
Department of Chemistry

A general study is being made of those photophysical properties of organic molecules that have relevance in determining their radiation-chemical behavior. Projects currently in progress include: (a) A study of the effect of perfluoroalkanes to scavenge electrons generated by photoionization of solute molecules in nonpolar condensed phases. The effect is manifested by a reduction in photoionization current and in intensity of ion + electron recombination fluorescence. (b) A study of the effect of perfluoroalkanes to quench the fluorescence of Rydberg states of saturated hydrocarbon liquids by virtue of a charge transfer to the perfluoroalkane. New charge-transfer absorption bands have also been observed and studied in the course of this work. (c) Measurement of the electron impact energy-loss spectra of some hydrocarbon molecules to assist in the characterization of their electronic states.

Photochemical and Radiation Sciences, continued

DREXEL UNIVERSITY
Philadelphia, Pennsylvania 19104

216. A STUDY OF PHOTSENSITIZED REDOX REACTIONS IN MICROEMULSIONS	\$110,000	01-01
Raymond A. Mackay	24 mo.	
Department of Chemistry	FY81-82	

The objective of this research program is to probe the utility of microemulsions in solar energy conversion systems. The photoreduction of adsorbed dye is being used as a test system to examine the effect of microemulsion type, pH, reaction product(s) and sensitizer on the quantum yield. The principal test system is the methyl red (oxidant)-ascorbate (reductant) couple. Other systems are being developed to explore the role of reagent location within the interfacial region of the microdroplet. The sensitizers being employed are chlorophyll a, other chlorins, and a number of synthetic porphyrins including derivatives of tetra(pyridyl and carboxy)phenyl porphin. Mechanistic flash photolysis studies and photo-galvanic studies employing reversible redox couples are in progress.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

217. ENERGETICS OF THE FORMATION AND REACTIONS OF GASEOUS IONS	\$75,000	01-01
G. G. Meisels		
Department of Chemistry		

The principal purpose of this investigation is the establishment of potential energy surfaces and related energetic information describing the formation, rearrangement (isomerization), fragmentation, and collision reactions of gaseous ions of small organic molecules. Experimental approaches rely principally upon the detection of only those ions produced by energy selected photons whose formation is accompanied by ejection of near-zero energy electrons, thus defining the internal energy of the ion within 20 meV. Other methods include high resolution collision induced MS, and high pressure MS employing a small drift tube as the ion source. Reactions of some ions appear to involve electronic states which do not convert to vibrationally excited states of the ground electronic state. Thus energetic barriers to fragmentation and isomerization may be larger than those expected on the basis of adiabatic ground-state thermodynamics. Ion structures are also probed using structure-specific ion-molecule reactions. Systems under investigation include the $C_4H_8^+$ and CH_3ONO^+ and $CH_3NO_2^+$ isomers.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF NORTH CAROLINA
Chapel Hill, North Carolina 27514

218. ENERGY CONVERSION PROCESSES BASED ON MOLECULAR EXCITED STATES \$84,000 01-01
Thomas J. Meyer
Department of Chemistry

The research effort is based on the study and exploitation of excited states of transition metal complexes. It consists of parallel efforts in several different areas including: 1) The photochemistry and photophysical properties of the excited states including spectral assignments, identification of decay pathways; and the application of radiationless decay theory. 2) The synthesis of new series of emitting excited states based on Os(II) and Re(I). 3) The preparations and properties of metallopolymers containing metal complex chromophores. 4) Mechanistic details of the oxidation and reduction of water. 5) Electron and energy transfer processes of the excited states including applications in photochemical and photoelectrochemical energy conversion processes.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

219. FLASH PHOTOELECTROCHEMICAL STUDIES OF TRANSIENT ELECTRODE PROCESSES IMPORTANT IN SOLAR ENERGY CONVERSION \$66,000 01-01
Sam P. Perone
Department of Chemistry

It is the objective of this research program to apply electroanalytical and spectroscopic measurement techniques to the study of transient photolytic, photoemission, and photoelectrolytic processes associated with UV-visible irradiation of an electrode/solution interface. Both semiconductor and metallic electrodes are being employed. Because these studies are particularly concerned with the characterization of transient phenomena, the general methodology of flash photolysis is employed (including both xenon flash lamp and tuneable pulsed dye laser sources). The novel perspective afforded by transient electroanalytical/spectroscopic measurements of photoinitiated electrode processes should allow more definitive mechanistic studies of solar conversion phenomena. Most recently it has been shown that 10 nsec time resolution can be obtained in these studies.

Photochemical and Radiation Sciences, continued

CLEMSON UNIVERSITY
Clemson, South Carolina 29631

220. INTRAMOLECULAR ENERGY TRANSFER REACTION AS A METHOD FOR METAL COMPLEX ASSISTED PRODUCTION OF HYDROGEN	\$72,900 24 mo. FY80-81	01-01
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John D. Petersen
Department of Chemistry

This program is designed to develop an understanding of excited state energy transfer reactions in mixed-metal, transition metal dimer systems. Current model systems employ the binding of highly absorbing, yet unreactive, metal centers of Fe(II) and Ru(II), bridged through N-heterocyclic ligands, to reactive metal centers of Co(III) and Rh(III). Conventional photochemical techniques are used to study the efficiency and mechanism of the energy transfer process. Thermal kinetic and equilibrium studies describe the stability constraints of the dimer complexes, while electrochemistry and ^{57}Fe Mössbauer spectroscopy are being used to determine ground/excited state changes in the dimer complexes with respect to the monomeric fragments. Variations in the bridging ligand are used to study the effectiveness of metal-metal communication in terms of excited state energy modifications and the efficiency of the energy transfer process.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

221. HIGH ENERGY HALOGEN REACTIONS ACTIVATED BY NUCLEAR TRANSFORMATIONS	\$112,700 24 mo. FY81-82	01-01
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Edward P. Rack
Department of Chemistry

The fundamental 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 of single chiral center molecules, systematics, mechanisms and iodine reactivity in a collapsing molecular environment and caging of halogen hot atoms in an ice lattice are under investigation. Practical applications of hot atoms chemistry to activation analysis for trace elements or molecules in biological systems, to radiopharmacy involving synthesis and radioprotection, and to the study of solute-solute and solute-solvent interactions of dilute solutions of biological molecules are being carried out.

Photochemical and Radiation Sciences, continued

CARNEGIE-MELLON UNIVERSITY
Pittsburgh, Pennsylvania 15213

222. PHOTODECOMPOSITION OF WATER IN HOMOGENEOUS SOLUTION	\$60,009 15 mo. FY 80-81	01-01
Robert M. Richman Department of Chemistry		

The goal of this project is to study the chemical, photochemical, and electrochemical behavior of compounds that are likely to be useful in solar energy conversion. Mechanisms of energy storage other than redox quenching of long-lived excited states are sought. One line of inquiry follows the photochemistry of dioxomolybdenum compounds, which have the cis-MoO₂⁺ moiety. Detailed studies of the kinetic pathways following irradiation of the dithiocarbamate, benzacac, and porphyrin compounds are being pursued. The goal here is to find conditions under which oxygen will be liberated. A second line of inquiry seeks examples of photodisproportionation reactions. Dimers which, upon irradiation, yield strong oxidants and/or reductants could be used in energy storage schemes. Several manganese, molybdenum, and ruthenium dimers are being pursued for their potential to do this photochemistry.

THE JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

223. FAR INFRARED CHEMICAL LASERS	\$56,000	01-01
Dean W. Robinson Department of Chemistry		

This research is concerned mainly with the pumping of submillimeter lasers by reaction and energy transfer. Rates of formation of inverted populations are determined through observation of the time evolution of the stimulated emission. Having reported formerly on the pure rotation OH and NH lasers, this year is concerned with the HF case. Rotational inversions are produced in vibrational states $v=0$ to $v=8$ through $V \rightarrow R$ energy transfer. The vibrational excitation is the result of various chemical reactions by which the HF is formed. Pure rotational lasing is observed between several high (typically $J=9-14$) rotational levels in each of the above vibrational states. Work is also in progress on the newly discovered flash pumped gas lasers H₂O (lines near 100 cm^{-1}) and HCN (30 cm^{-1}). The former is superfluorescent and exhibits quantum beats while the latter is briefly superradiant. Inter and intramolecular energy transfer is also involved in the production of population inversions. These rates and mechanisms are under investigation.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF CALIFORNIA/DAVIS
Davis, California 95616

224. NUCLEAR METHODS IN CHEMICAL KINETICS \$63,996 01-01
John W. Root
Department of Chemistry

The central objective of this research program involves the elucidation of non-equilibrium kinetic phenomena. The high energy chemical processes that accompany cyclotron induced nuclear reactions are being probed with emphasis on the reactions with halocarbon substrates of recoiling ^{18}F and ^{39}Cl atoms produced via the $^{19}\text{F}(n,2n)^{18}\text{F}$ and $^{40}\text{Ar}(n,pn)^{39}\text{Cl}$ processes. Radiolabeled product analysis is accomplished using conventional radiochemical separations as well as radio gas chromatography. The results include mechanisms and relative rates of formation for the labeled organic and inorganic reaction products, and internal excitation energy distributions for the products from energetic atomic substitution reactions. The kinetic behavior of ^{14}C -labeled excited halocarbons activated by photoinduced exoergic chemical reactions is also under investigation. These latter studies are expected to allow improved testing of the available theoretical models for collisional energy transfer by chemically activated species.

UNIVERSITY OF CALIFORNIA/IRVINE
Irvine, California 92664

225. RESEARCH IN CHEMICAL KINETICS \$155,000 01-01
F. Sherwood Rowland
Department of Chemistry

Radioactive halogen atoms (^{18}F , ^{38}Cl) are produced by nuclear reactions, thermalized by multiple collision with an inert parent molecule (SF_6 , CClF_3), and reacted with various substrate molecules present in low mole fraction in the gas phase. The abstraction of H atoms from CH_4 or CH_3Cl by ^{38}Cl shows a strong temperature dependence between 240-360K, indicative of the thermal character of such reactions. Rapid substitution reactions are observed for many organometallic substances, with the displacement of the metal at the C-M bond ($\text{X} + \text{R}_4\text{M} \rightarrow \text{RX} + \text{R}_3\text{M}$, with $\text{X}=\text{F}, \text{Cl}$; $\text{M}=\text{Pb}, \text{Sn}, \text{Ge}$; $\text{R}=\text{CH}_3, \text{CH}_2=\text{CH}$, etc.). Addition reactions at multiple bonds (e.g. $\text{CF}_3\text{C}\equiv\text{CH}$) provide information about central vs. terminal addition, and cis/trans ratios in the radicals. Pressure-dependent studies show radical decomposition rates for many radicals of $\sim 10^8\text{-}10^9\text{s}^{-1}$. Absolute calibrations continue for trace atmospheric gases.

Photochemical and Radiation Sciences, continued

WORCESTER POLYTECHNIC INSTITUTE
Worcester, Massachusetts 01609

226. THE GAS PHASE RADIOLYSIS AND VACUUM ULTRAVIOLET PHOTOLYSIS OF HETEROCYCLIC ORGANIC COMPOUNDS Alfred A. Scala Department of Chemistry	\$78,483 24 mo. FY 81-82	01-01
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This research is designed to provide basic information concerning the interactions between high energy radiation and heterocyclic organic compounds. Both vacuum ultraviolet photons and ^{60}Co γ -rays are used as energy sources and reactions of neutral and ionic species are examined. Results on a series of heterocycles indicate that for gas phase systems, generalizations concerning the modes of reaction of these molecules, based upon thermodynamic factors, are possible. These generalizations permit the prediction of reaction modes for molecules yet to be studied. Recent investigations of the condensed phase photochemistry of a number of heterocycles has produced results which seem to indicate that, either some of the excited states produced in these systems can be quenched, or most of the products observed in gas phase systems are actually the result of secondary decompositions of the primary products.

CHARLES F. KETTERING RESEARCH LABORATORY
Yellow Springs, Ohio 45387

227. PARTICULATE MODELS OF PHOTOSYNTHESIS Gilbert R. Seely	\$55,000	01-01
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The program consists of the investigation of photophysical and photochemical properties of chlorophyll, adsorbed together with other amphiphilic molecules to particles of polyethylene swollen with low molecular weight hydrocarbon diluents. When suspended in aqueous media, the particles are intended to provide a viscous medium for anchorage of the hydrophobic parts of amphiphilic molecules. In general, chlorophyll is maintained in monomeric form in the presence of amphiphiles that interact with it, such as alkylamides, or as fluorescent dimers or higher aggregates at greater concentration. Specific aspects under investigation include adsorption isotherms of chlorophyll and surfactants, resolution of absorption and fluorescence spectra into their components as a function of concentration and temperature, and energy transfer among chlorophyll species and to traps. The photochemistry of chlorophyll in these systems is being examined with particular regard for the distribution of oxidants and reductants between the aqueous and particle phases.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

228. DYNAMICS AND MECHANISMS OF CATALYTIC PROCESSES AND HOT CHEMISTRY \$83,000 01-01
Leonard D. Spicer
Department of Chemistry

This research is designed to explore reaction kinetics, atomic and molecular collision dynamics, and energy transfer in thermal, photochemical, and hot reactions. Initial results of a study of photo-assistance in catalytic hydrogenation with Wilkinson's Catalyst have been reported. Major features observed include a markedly increased rate for hydrogenation of cyclohexene and 1-hexene during irradiation and a modification of selectivity which initiates isomerization of 1-hexene to 2-hexene during and after irradiation. The dynamical model developed in this laboratory to describe recoil processes has been applied to a preliminary investigation of the moderated nuclear recoil technique for measuring thermal rate constants. The general applicability and constraints of the technique have been identified and a criterion has been developed to select the method of analysis which yields the most accurate relative thermal rate constants. The new reaction between sulfur dioxide and hexamethyldisilazane discovered in this laboratory has been characterized further. The stoichiometry and mechanism for this acid-base reaction are being investigated.

PRINCETON UNIVERSITY
Princeton, New Jersey 08544

229. PHOTOELECTROCHEMISTRY WITH CHEMICALLY MODIFIED ELECTRODES \$130,000 01-01
24 mo.
Thomas G. Spiro FY81-82
Department of Chemistry

Electroactive films of variable thickness, formed by electropolymerization or silinization reactions, are being studied with respect to their ground and excited state electron transfer properties, and stability. Bipyridyl and o-phenanthroline complexes of ruthenium (II), with vinyl groups attached at various points on the ligands, and transition metal complexes of protoporphyrin IX, are used in forming films under controlled conditions. The films are characterized voltametrically and with various physical and chemical techniques. Photoelectroactivity is checked with wide band-gap semiconductor electrodes (SnO_2 and TiO_2).

Photochemical and Radiation Sciences, continued

MOUNT HOLYOKE COLLEGE
South Hadley, Massachusetts 01075

230. PHOTOELECTROCHEMISTRY OF ORGANIC DYES \$56,400 01-01
Mark T. Spitler
Department of Chemistry

This project seeks to determine the role of electron transfer in the quenching of the excited states of organic dyes adsorbed at electrode surfaces. An attenuated total reflection technique is used to enable in situ determinations of the quantum efficiency of current producing photoreactions at both metal and semiconductor surfaces. Photooxidation of dyes at ZnO and TiO₂ surfaces is being studied with series of cyanine, merocyanine, and oxanine dyes varied to demonstrate the effect of redox potential, excitation energy, molecular structure, and charge on the electron transfer from the excited state of the dye to the conduction band of the semiconductor. Photoassisted oxidation of dyes at Pt electrodes is also being investigated with these dyes. Estimation of the degree of excitation quenching caused by this oxidation is allowed through concomitant measurements of the fluorescence intensity of the adsorbed dye.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

231. HOT ATOM REACTIONS INVOLVING \$50,000 01-01
MULTIVALENT AND UNIVALENT SPECIES
Yi-Noo Tang
Department of Chemistry

The purpose of this research is to study the reactions of various types of energetic atoms and the mechanism of catalytic hydrogenation. The most significant progress during this period is with the recoil ³¹Si systems. It is discovered that monomeric ³¹SiF₂ adds to two molecules of C₂H₄ to give 1,1-difluorosilacyclopentane as a final product. When radical scavengers are added, the yield of this product is not altered. This implies that, (i) the reacting ³¹SiF₂ is in its singlet ground electronic state, and (ii) the intermediate formed between ³¹SiF₂ and the first molecule of C₂H₄ must be molecular instead of radical in nature. For the hydrogenation experiments, the catalytic C-F hydrogenolysis of six fluorocarbons have been performed. The apparent activation energies and the A-factors have been evaluated.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF KENTUCKY
Lexington, Kentucky 40506

232. ELECTRON PHOTOEJECTION IN CARBANIONS \$45,000 01-01
Laren M. Tolbert
Department of Chemistry

Visible light causes resonance-stabilized carbanions to eject electrons at high potentials. Since such negatively charged species are easy to prepare and their chemistry is relatively uncomplicated, they serve as useful models for studying electron photoejection. The photoactive state of these species is readily quenched by simple aromatic hydrocarbons. Stern-Volmer quenching studies are being used to probe the oxidation potential and lifetime of the excited state, and the effect of structure and electronic properties on photoreactivity is being determined. Wavelength-dependent quantum yields are also being examined to ascertain the existence of a photoejection threshold in solution. The effect of gegenion and degree of solvation are also being investigated. The goal of this research is a clear understanding of the mechanism by which photostimulated electron transfer occurs in these simple systems so that more complex systems may be understood.

UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

233. MECHANISMS OF PHOTOCHEMICAL ENERGY \$60,000 01-01
CONVERSION BY CHLOROPHYLL
Gordon Tollin
Department of Biochemistry

The goals of this project are to elucidate the detailed mechanisms involved in light-induced one-electron transfer reactions involving chlorophyll and electron donors and acceptors, and 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. Studies are carried out in homogeneous fluid solutions, polymer films and lipid bilayers. Laser flash photolysis is used to measure yields and kinetics of transient intermediates such as excited states and radical products. We are developing fundamental information which can be used to devise strategies for increasing the yields of high energy products, to decrease the back reaction probability, and to facilitate secondary electron transfer to external donors and acceptors.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF MASSACHUSETTS/BOSTON
Boston, Massachusetts 02125

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| 234. INVESTIGATION OF THE STRUCTURE OF
PHOTOSYNTHETIC REACTION CENTERS
Hans van Willigen
Department of Chemistry | \$115,525
24 mo.
FY81-82 | 01-01 |
|---|--------------------------------|-------|

It is the purpose of the research to study the structure of the reaction center involved in the primary events in photosynthesis. Photoexcitation of the reaction center leads to the formation of triplet state molecules. These paramagnetic molecules are studied with the aid of electron nuclear double resonance (ENDOR) and electron nuclear triple resonance (TRIPLE). ENDOR and TRIPLE measurements give information on electron spin-nuclear spin hyperfine interactions in the triplet molecules. The data give an insight in the electronic as well as geometric structure of the reaction centers.

UNIVERSITY OF ILLINOIS/CHICAGO CIRCLE
Chicago, Illinois 60680

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| 235. EVALUATION OF THE ESE ENVELOPE MODULATION
TECHNIQUE FOR STUDIES OF FREE RADICALS
Robert I. Walter
Department of Chemistry | \$70,624
24 mo.
FY81-82 | 01-01 |
|---|-------------------------------|-------|

It is known that analysis of the electron spin echo envelope modulation can give precise information on the hyperfine parameters for dilute single crystals of paramagnetic species. The objective of this work is to determine whether the method can also yield useful data on free radicals in random glassy solution. The standard magnetic resonance techniques (EPR, NMR contact shifts, and ENDOR), together with isotopic labelling, are used to determine and assign the hyperfine parameters for a series of aromatic nitroxide free radicals selected and synthesized to provide increasing numbers of magnetically equivalent sets of deuterium, ^{14}N , or ^{15}N atoms. These well-characterized free radicals are then examined in a glassy matrix by the three-pulse electron spin echo technique by members of the photosynthesis group at the Argonne National Laboratory under the supervision of James Norris. The results are expected to indicate the range and precision of data which can be extracted from the electron spin echo envelope modulation by adjusting parameters to optimize fit to the modulation, or by Fourier transform methods.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

236. PHOTOINDUCED INTERACTIONS OF TRANSITION METAL COMPLEXES WITH WATER \$50,000 01-01
Richard J. Watts
Department of Chemistry

This program of research explores the chemical and physical consequences of light absorption by solvated transition metal complexes. Emphasis is placed on N-heterocyclic complexes of the group VIII B metal ions; some additional work is being done on organometallic group VII B metal complexes. A newly acquired Nd/YAG-pumped dye laser is being utilized to develop techniques to study chemical and physical excited state processes via excited state absorption, ground state bleaching, and transient absorption. These techniques are being applied to the characterization of rates and mechanisms of photo-substitution, photoinduced electron transfer, excited state proton transfer, and photophysical decay processes. Both mononuclear and binuclear metal complexes are presently under investigation. Bridging ligands which vary the metal-metal interaction are being used to explore the effects of this interaction on excited state chemical and physical decay processes.

UNIVERSITY OF NORTH CAROLINA
Chapel Hill, North Carolina 27514

237. APPLICATIONS OF PHOTOINDUCED ELECTRON TRANSFER AND HYDROGEN ABSTRACTION PROCESSES TO CHEMICAL AND ELECTROCHEMICAL CONVERSION PROCESSES \$130,000 01-01
24 mo.
FY81-82
David G. Whitten
Department of Chemistry

This research program involves studies of light-induced electron transfer and hydrogen atom abstraction processes occurring through excitation of chromophores absorbing visible and near ultraviolet light. During the current project period work is focused on two major areas. The first involves photoelectrochemical cells in which light-induced reaction of ketones and metalloporphyrins with alcohols and trialkylamines results in the formation of reduced radicals which are scavenged by Weitz-type reagents whose reduced forms are oxidized concurrent with generation of a reducing photocurrent. These studies have demonstrated thus far the generation of significant photocurrent concurrent with the driving of the net endothermic chemical reaction. The second area of emphasis concerns reactions of intensely colored dyes such as diacetylidigo, thioindigo, and monoreduced Weitz-type reagents with potential reductants. Efficient photoreduction and photoaddition processes have been observed in several cases. Applications of these reactions are being investigated.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

238. STUDIES IN HOT ATOM AND RADIATION CHEMISTRY \$29,885 01-01
J. E. Willard
Department of Chemistry

The objectives of this continuing project are to obtain a better understanding of the production, migration, trapping, reactions and spectra of free radicals, hydrogen atoms, electrons, and ions formed in solid organic matrices at 4 K - 200 K. The species studied are formed by irradiation with γ -rays, X-rays, and ultraviolet radiation. Electron spin resonance, ultraviolet, visible and infrared spectrometry are used for analysis. Current emphasis is on the reactions of hydrogen atoms, the role of neutralization processes in free radical production in radiolyzed hydrocarbons and the photolytic decomposition of free radicals (e.g. CH₃, CD₃, HCO) in CH₄, CD₄ and rare gas matrices at cryogenic temperatures.

UNIVERSITY OF TENNESSEE
Knoxville, Tennessee 37916

239. RESEARCH CONCERNING IONIC AND FREE RADICAL REACTIONS IN RADIATION CHEMISTRY AND PHOTOCHEMISTRY \$85,000 01-01
T. Ffrancon Williams
Department of Chemistry

This program is directed to the identification of novel free-radical intermediates and to the study of radical reactivity of low temperatures, mainly by means of electron spin resonance (ESR) spectroscopy. Radicals are produced by the irradiation of solids, this technique being particularly useful for the generation of a wide variety of radical ions. By a suitable choice of solid matrix, either radical cations or radical anions may be formed by electron removal from, or electron attachment to, suitable molecules. The electronic structures and geometries of high-energy species such as hydrocarbon (alkane) radical cations and fluorocarbon radical anions are of particular interest since the electron spin is delocalized in the σ framework of these radicals. These species are being studied by measurements of the hyperfine coupling constants, including those for ¹³C-labeled radicals. The chemical reactivity of radicals in hydrogen-atom and proton transfer reactions is also being investigated. Research is also underway on the role of paramagnetic species in organometallic photochemistry.

Photochemical and Radiation Sciences, continued

The following eight contracts are technically monitored by the Solar Energy Research Institute under the SERI University Research Program, and are funded by the Division of Chemical Sciences. For further information about this program, contact Dr. Alex Kotch, Manager, University Programs Office, SERI, 1536 Cole Boulevard, Golden, Colorado 80401. Telephone 303-231-1823 or FTS 327-1823.

WESTERN CONNECTICUT STATE COLLEGE
Danbury, Connecticut 06810

241. PHOTOELECTROCHEMICAL STUDIES ON CHLORINS, PORPHYRINS, AND THEIR METALLODERIVATIVES \$24,980 01-01
Alan D. Adler
Department of Chemistry

The objective of this research is to elucidate the effects of structural variations, solution conditions, and cell composition on the photoelectrochemical behavior of chlorins, porphyrins, their metalloderivatives, and related structures. Cyclic voltammetry, pulse polarography, and spectrophotometry are employed to investigate these cell processes. Observed half-wave potentials show strong concentration variation indicating aggregative phenomena. They also vary with nature of the counterions present, especially for the one-electron steps, indicating ion-pairing phenomena. Such behavior is suggestive of possible control mechanisms in photosynthesis and indicates possible modes of utilizing or employing these materials in synthetic solar conversion devices and processes.

UNIVERSITY OF DELAWARE
Newark, Delaware 19711

242. PHOTOSENSITIVE MOLECULAR ARRAYS: A STUDY OF SYNTHETIC METHODS, PHOTOELECTRIC PROPERTIES, AND ENERGY TRANSFER MECHANISMS \$64,706 01-01
John E. Bulkowski
Department of Chemistry

The basic objective of this project is the preparation of a novel photosensitive molecular film to be used to construct a photoelectrochemical cell for the conversion of sunlight into electricity or fuels. The synthetic technique involves assembling specially designed surfactant metalloporphyrin dyes as an ordered monolayer on the cell's electrode surface. Subsequent reaction at the metal sites of the first template layer allows formation of successive dye layers one layer at a time. The resulting organization contains chains of metals interconnecting the dye layers providing a pathway for electron transfer from the excited centers to the electrode surface. A significant feature of this method arises from the ability to specifically tailor the film's structure on a molecular level. The electrical and optical properties of these dye sensitized electrodes are under investigation to determine their photoelectric and energy transfer properties as a function of dye orientation and film structural parameters.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF SOUTHERN MISSISSIPPI
Hattiesburg, Mississippi 39401

243. PHOTOGALVANIC CELLS DRIVEN BY ELECTRON TRANSFER QUENCHING OF EXCITED SINGLET STATES \$49,126 01-01
David Creed and Newton C. Fawcett
Department of Chemistry

The goal of this project is to develop more quantum efficient photogalvanic cells for conversion of light into electricity. Both photochemical and electrochemical aspects of the problem are under study. The photoreduction of the dye oxonine by Fe(II) occurs directly from the singlet state of the dye. A photogalvanic cell based on this reaction is being developed as a singlet-state driven analogue of the well studied triplet-state driven thionine/Fe(II) cell. In the oxonine/Fe(II) cell low power conversion efficiencies are partly attributed to the low probability of net electron transfer from Fe(II) to oxonine singlet state. Attempts are being made to understand this effect and improve net quantum efficiencies. Some novel dyes have been synthesized with greatly improved water solubility and aggregation characteristics relative to thionine and methylene blue. The photoreduction of these dyes by Fe(II) is being studied by steady-state and laser flash photolysis techniques. Several promising new cells based on these dye/Fe(II) systems are under investigation.

THE OHIO STATE UNIVERSITY
Columbus, Ohio 43210

244. A FLAVIN MONONUCLEOTIDE-PHOTOSYSTEM I SOLAR BATTERY \$60,500 01-01
Elizabeth L. Gross
Department of Biochemistry

This research program is designed to develop a solar battery (photoelectrochemical cell) using both photosynthetic electron transport and the direct photoreduction of the electron acceptor (flavin mononucleotide; FMN). Progress to date includes a power conversion efficiency of 4%, a power of 2000 μ watts ($2\text{W}/\text{m}^2$), a short circuit current of 15mA and an open circuit potential of 7-800mV. The effect of varying the electron acceptors, donors and other chemicals is being investigated as is the use of different electrode materials and changes in cell design.

Photochemical and Radiation Sciences, continued

ARIZONA STATE UNIVERSITY
Tempe, Arizona 85281

245. ENHANCED SOLAR ENERGY COLLECTION IN
PORPHYRIN BASED PHOTOCONVERSION SCHEMES
Devens Gust and Thomas A. Moore
Department of Chemistry
- \$70,520 01-01

Carotenoid polyenes are found in the photosynthetic apparatus of green plants where they perform both an antenna function (singlet energy transfer to chlorophyll) and a photoprotective function (both quenching the chlorophyll triplet to prevent sensitization of singlet oxygen and scavenging singlet oxygen). Synthetic solar energy conversion systems based on chlorophylls or porphyrins will also require photoprotection and antenna function for stable, efficient operation. The approach to this problem used here is to prepare and study synthetic carotenoporphyrins in an attempt to mimic the important features of the complex natural carotenoid-chlorophyll-enzyme-membrane supra-molecular structure. Such biomimetic carotenoporphyrins have now been prepared. Approximately 25 percent efficient singlet energy transfer from the carotenoid moiety to the porphyrin has been achieved concomitant with 100 percent suppression of singlet oxygen sensitization. In addition, there is evidence that carotenoporphyrins may also be able to function in the photo-production of stable high energy chemical species.

UNIVERSITY OF GEORGIA
Athens, Georgia 30602

246. DEVELOPMENT OF A PHOTOCHEMICAL ENERGY
STORAGE SYSTEM
Richard R. Hautala and Charles Kutal
Department of Chemistry
- \$79,600 01-01

A solar energy storage system based upon the interconversion of norbornadiene (NBD) and quadricyclene (Q) possesses several attractive features, including high specific energy storage capacity, long-term kinetic stability of the energy rich photoproduct at ambient temperatures, and relatively inexpensive reactants. Two steps are required in this cyclical system: (1) Energy storage through the sensitized photolysis of NBD to Q in an endothermic reaction; (2) Energy release through the catalyzed reversion of Q to NBD in an exothermic reaction. The purpose of this research program is the exploration of several fundamental areas which are related to the development of the NBD-Q energy storage system. Specifically, the following are under study: a) detailed studies of the properties of several sensitizers, particularly with regard to the mechanism of sensitization; b) development of catalysts with high activity and specificity, long life-time and low cost; and c) examination of the feasibility of using various immobilized sensitizers and catalysts in the energy storage and release steps of the system.

Photochemical and Radiation Sciences, continued

COLORADO STATE UNIVERSITY
Fort Collins, Colorado 80523

247. SOLAR-CHEMICAL ENERGY CONVERSION VIA REVERSIBLE LIQUID PHASE DIELS-ALDER REACTIONS \$53,318 01-01
Terry G. Lenz and Louis S. Hegedus
Department of Agriculture and
Chemical Engineering

Conversion of intermittent solar energy to a chemical form via reversible liquid phase Diels-Alder reactions is a promising means of storing and transporting this important energy source. Knowledge of control over equilibrium (for maximum $|\Delta H_r^\circ|$) requires a firm understanding of the limits and origin of $|\Delta S_r^\circ|$ for these condensed phase reactions. Studies to date are very encouraging in that they quantify the large effect that substituents have on reaction equilibrium. For example, the anthracene/maleic anhydride system (in trichlorobenzene) has a T^* (where $K_{eq} = 1$) of 464°C for $|\Delta H_r^\circ| = 90.4$ kJ/mol, which is high relative to the thermal stability of organic molecules. However, the system 9-phenylanthracene/maleic anhydride has a T^* of 253°C , while anthracene/isopropyl maleic anhydride has a T^* of 200°C , with $|\Delta H_r^\circ|$ in the 90-100 kJ/mol range. These experimental results, plus theoretical calculations suggest that the origin of the T^* variation is quenching of substituent rotation upon condensation to the Diels-Alder adduct. These results will be very helpful in systematic future identification of ideal liquid-phase Diels-Alder systems.

CALIFORNIA STATE UNIVERSITY/ FULLERTON
Fullerton, California 92634

248. SOLAR ENERGY STORAGE VIA ENDOTHERMIC PHOTO-CHEMICAL REACTIONS \$42,931 01-01
John Olmsted III and Carl C. Wamser
Department of Chemistry

Investigations are continuing on the potential for solar energy storage of several unimolecular photoisomerization reactions. The photoisomerizations of aromatic molecules to their Dewar analogues, the trans-cis photoisomerization about the aromatic azo linkage, and sensitization of the isomerization of norbornadiene to quadricyclane are being given particular attention. Energy storage potential is directly determined using a photomicrocalorimeter, which assays the fraction of incident photon energy converted to chemical energy. Possibilities are also being explored for enhancing the efficiency of suitable photoisomerization reactions by utilizing photosensitizers, in particular polymer-bound photosensitizers which permit easy separation of the energy storage phase from the sensitizer.

Chemical Physics

SRI INTERNATIONAL
Menlo Park, California 94025

249. ENERGY TRANSFER STUDIES USING LARGE, \$69,900 01-02
HIGHLY VIBRATIONALLY EXCITED MOLECULES
John R. Barker and G. P. Smith
Department of Chemical Kinetics

Energy transfer among large molecules is of crucial importance in many areas, including the pyrolysis of fuels and in laser-induced isotope separation schemes. Experiments are underway to answer several fundamental questions about energy-transfer: Does the average amount of energy transferred per collision depend on the initial vibrational energy in the molecule? How does the average amount of energy transferred depend on the identity and temperature of the collider gas? Laser excitation is used to prepare excited molecules with known and controlled amounts of internal vibrational excitation. Time-resolved infrared fluorescence is used to monitor the collisional de-excitation of the excited molecules and computer simulations are used to analyze the data. The results are very promising and show good correspondence with the limited data available from other experimental techniques.

CORNELL UNIVERSITY
Ithaca, New York 14853

250. STUDIES OF THE COMBUSTION OF MODEL FUELS \$55,000 01-02
WITH LOW HYDROGEN CONTENT 20.5 mo.
Simon H. Bauer FY80-81
Department of Chemistry

The strategy upon which this investigation is based calls for a comparative study of the pyrolysis, oxidation and soot production of a five member sequence of fuels with low H/C ratios, selected to represent major hydrocarbon components which have been identified as structural units in coals. The first step is the determination of the temperature dependence of product distributions upon their pyrolysis (under large Ar dilution) in a single-pulse shock-tube. The rate constants for their degradation are to be determined, as well as conditions for the onset of soot production in these fuel/argon mixtures. The exo-endo thermic balance during the initial stages of pyrolysis will be measured (in a second shock-tube) from schlieren deflection of a laser beam by the post-shock front density-gradient. To augment the initiation of chain reactions controlled levels of highly reactive radicals will be introduced by incorporating readily decomposed precursors with the fuels. The relative rates of attack by oxygen atoms will be investigated in a high temperature flow-tube reactor coupled to a quadrupole mass analyzer.

Chemical Physics, continued

THE UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

251. FINITE-TIME THERMODYNAMICS \$60,000 01-02
R. Stephen Berry
Department of Chemistry and the James
Franck Institute

This research extends concepts and methods of thermodynamics to the global description of processes whose definitions include constraints on rates or times. The concept of available work or availability has been extended, in recent work, to such processes, even when the initial states of the working system is not in internal equilibrium. The role of generic models has been examined in some detail for processes with time or rate constraints, and a theorem has been proved, in which sufficient conditions are given for the work done by an optimized generic model to be an upper bound for the work done by any real process being judged against that generic model. One generic model of wide applicability has been worked out in detail, and is shown to have a constant of motion.

COLUMBIA UNIVERSITY
New York, New York 10027

252. ENERGY PARTITIONING IN ELEMENTARY GAS \$68,000 01-02
PHASE REACTIONS
Richard Bersohn
Department of Chemistry

In an exothermic reaction energy is released into electronic, vibrational, rotational and translational degrees of freedom of the products. The purpose of this research is to study the simplest possible chemical reactions of the classic form $A + BC \rightarrow AB + C$ by photogenerating the atom A in the midst of a low pressure gas of BC molecules. The experiment requires two lasers, an excimer laser to generate the atom A which may be carbon, hydrogen or fluorine atoms, and a dye laser to excite fluorescence of AB molecules, C atoms or both. The fluorescence excitation spectrum of the molecule AB yields the populations of the different ground vibrational and rotational states. If the atom C is sufficiently light, the shape of the Doppler profile of the atomic absorption provides a measure of the translational energy distribution of the atom and consequently of the internal energy distribution of the AB molecule.

Chemical Physics, continued

ILLINOIS INSTITUTE OF TECHNOLOGY
Chicago, Illinois 60616

253. THEORETICAL STUDIES OF COMBUSTION DYNAMICS \$54,335 01-02
Joel M. Bowman
Department of Chemistry

The objective of this research program is the accurate calculation of rate constants for elementary bimolecular reactions of importance in the combustion of hydrogen and hydrogen containing fuels. The approach taken is based on using the latest ab initio calculations of potential energy surfaces and approximate quantum mechanical scattering calculations. The reactions $O(^3P)+H_2 \rightarrow OH+H$ and $O(^3P)+HD$ (for both ground state and vibrationally excited H_2 and HD) are being studied by collinear exact quantum dynamics with an adiabatic treatment of the OH_2 bending motion. The calculated rate constants will be the most accurate theoretical ones ever calculated. Work is beginning on the development of a collinear-type exact quantum diatom-diatom code which will be applied to the $OH+H_2$ reaction in the near future.

YALE UNIVERSITY
New Haven, Connecticut 06520

254. SIMULTANEOUS MULTIPOINT MEASUREMENTS OF DENSITY GRADIENTS AND TEMPERATURE IN A FLAME \$63,000 01-02
R. K. Chang, B. T. Chu, and M. B. Long
Department of Engineering and Applied Science

Turbulence enhances the mixing of heterogeneous fuel and oxidant gases and affects the overall chemical reaction rates as well. For turbulent flow, where the scales of the energy-containing eddies are much larger than the flame sheet thickness, the turbulent eddies can be expected to wrinkle, distort, fold, convolute, and fragment the flame sheet. We propose to study the turbulent reacting flows by nonintrusive in situ optical diagnostic techniques. By extending our Lorenz/Mie scattering experiment in a cold flow, we plan to measure the instantaneous concentration distribution and concentration gradient in a plane within the flame. By extending our BOXCARS experiment with a broadband dye laser, we intend to measure the instantaneous temperature and concentration from each point along a line within the flame. These instantaneously determined spatial distributions, together with their joint pdf, provide critical information for testing several existing turbulent combustion theories and for constructing new theories which may be suggested by our data.

Chemical Physics, continued

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

255. UNIMOLECULAR DECAY DYNAMICS OF INTERNAL ENERGY SELECTED MOLECULES F. Fleming Crim Department of Chemistry	\$100,320 24 mo. FY 81-82	01-02
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This program 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 combined with time resolved spectroscopic detection. Application of the visible chemiluminescence detection technique to the decomposition of a cyclic peroxide (tetramethyldioxetane) has produced CH overtone vibration excitation spectra of very low pressure samples, directly measured the unimolecular decay rate of a state-selected molecule, and revealed the presence of a previously unobserved luminescent decomposition product. Current work will extend these measurements to include state-resolved product detection.

SRI INTERNATIONAL
Menlo Park, California 94025

256. COMBUSTION RESEARCH PROGRAM: FLAME STUDIES, LASER DIAGNOSTICS AND CHEMICAL KINETICS David R. Crosley Molecular Physics Laboratory	\$100,364	01-02
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This research program involves a combination of laser spectroscopic techniques [chiefly, laser-induced fluorescence (LIF)], and chemical kinetics measurements to investigate the chemistry of combustion processes. The research comprises several related parts: (i) the probing of flat flames using LIF to measure profiles of radicals such as OH, NH, NH₂, CN, HNO, etc., important as chemical intermediates; (ii) an isothermal laser pyrolysis (ILP) experiment, in which reactants are rapidly heated through absorption (by SF₆ seeded in the mixture) of CO₂ laser radiation, with LIF measurements of radicals are made as a function of time; (iii) computer modeling of the chemical networks of the flame and ILP experiments; (iv) development of a LIF spectroscopic and collisional data base suitable for quantitative detection of important species; (v) flow system rate constant and product measurements for key reactions; (vi) development and application of rate constant estimation methods. The systems under study are NH₃/O₂, CH₃NH₂/O₂, CH₄/NH₃/O₂, and C₃H₈/NH₃/O₂, whose chemistry is important in NO_x formation in combustion systems.

Chemical Physics, continued

WILLIAM MARSH RICE UNIVERSITY
Houston, Texas 77001

257. INFRARED ABSORPTION SPECTROSCOPY WITH COLOR CENTER LASERS \$57,000 01-02
Robert F. Curl
Department of Chemistry

The overall aim of this research program is to develop high sensitivity, high resolution methods of 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. One absorption spectroscopy method using the magnetic rotation effect to balance out source noise has already been developed and used to detect the fundamental absorption of OH. Present work focuses on the parallel development of a Zeeman modulated long pass absorption cell which can be adapted for magnetic rotation. This apparatus will be used to study the spectra of small free radicals such as CH₃, C₂H, HO₂ and NH₂. Another method being developed is aimed at situations where Zeeman modulation is not possible and uses frequency modulation of the source with the molecular absorption acting as a discriminator. The source frequency modulation will be introduced by means of phase modulation using an electro-optic crystal.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

258. LASER PHOTOELECTRON SPECTROSCOPY OF IONS \$53,000 01-02
G. Barney Ellison
Department of Chemistry

Laser photoelectron spectroscopy is being used to study a large number of negative ions. This type of experiment provides direct, reliable thermodynamic information for ions and radicals such as electron affinities and bond dissociation energies. These data are crucial for an understanding of combustion processes and the atmospheric chemistry of air pollution. Specific ions of study are CH₂N⁻, CH₂CN⁻, C₃⁻, C₂O⁻, and HO₂⁻.

Chemical Physics, continued

UNIVERSITY OF OREGON
Eugene, Oregon 97403

259. LASER SPECTROSCOPY OF COMBUSTION INTER-
MEDIATES \$45,000 01-02
P. C. Engelking
Department of Chemistry

Laser induced fluorescence techniques are being used to measure the electronic spectra of molecular radicals that are found in combustion systems. A fast flow system utilizing fluorine atoms in a rare gas carrier prepares for study species such as methoxyl, CH_3O , and other alkoxy species. The identification and characterization of the spectra of these molecular radicals allows the understanding of their internal structure, and also provides the needed spectroscopic information basic to the detection and identification of these combustion intermediates in actual flame environments. In addition to the laser induced fluorescence studies, a number of metastable molecular radicals have been prepared in electric discharges in the fast flow apparatus. Spin changing intersystem transitions of these metastables are observed, providing thermochemical information and geometry information otherwise unavailable on these species. An example of this is the recent observation of the $\text{CF a}^4\Sigma^- - \text{X}^2\Pi$ system now being analyzed. Other such transitions are being sought.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

260. INFRARED LASER INDUCED ORGANIC REACTIONS \$50,190 01-02
William E. Farneth
Department of Chemistry

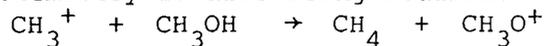
This project is an investigation of the potential and present utility of high power, infrared lasers for initiating and directing chemical reactions of organic molecules. The bulk of the work carried out thus far has examined reaction yields and product ratios from CO_2 -laser-induced decompositions of small organic molecules in the gas phase. Examination of branching ratios is an especially sensitive method for obtaining information about energy distributions among the laser-activated reactants. Particularly informative systems possess well-defined thermal chemistry, more than one accessible chromophore, and competitive decomposition routes of comparable energy. Systematic studies of vinylcyclopropane, bicyclopropyl- d_5 and diethylcarbonate- d_5 are underway. Using mechanistic information derived from these studies two specific applications of multiphoton IR activation are being examined. These are: (1) laser-induced heterogeneous reactions at gas/solid surfaces, and (2) laser-induced chemiluminescence.

Chemical Physics, continued

UNIVERSITY OF ROCHESTER
Rochester, New York 14627

261. LOW ENERGY ION-MOLECULE REACTIONS AND CHEMIONIZATION KINETICS \$56,000 01-02
James M. Farrar
Department of Chemistry

The goal of this research program is to achieve an understanding of the dynamics of important reactions of gas phase cations pertinent to combustion processes. The technique employed is molecular beam scattering, in which product energy and angular distributions are measured as a function of reagent translational energy from 0.5 eV to 10 eV. Emphasis is being placed upon proton transfer reactions of HCO^+ with a variety of molecules such as CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, HCHO , HCOOH and CH_3OCH_3 . The reaction of HCO^+ with H_2O to yield H_3O^+ , an extremely important flame ion, is also being studied at present. At relatively high collision energies, products of these proton transfer reactions become unstable toward dissociation; emphasis is being placed upon understanding the unimolecular decay dynamics of these fragmentation pathways. Because of the high stability of CH_3^+ , its combustion chemistry is also being studied. The hydride transfer reactions



are being examined in detail.

AEROCHEM RESEARCH LABORATORIES, INC.
Princeton, New Jersey 08540

262. EXPERIMENTAL DETERMINATION OF RATE COEFFICIENTS FOR IMPORTANT COMBUSTION/FUEL CONVERSION REACTIONS BY A NOVEL HIGH-TEMPERATURE PHOTOLYSIS TECHNIQUE \$85,000 01-02
William Felder

The aim of this project is to measure the rate coefficients and their temperature dependences of isolated, elementary free radical reactions which are of key importance in combustion and pollutant formation (or destruction) processes of fossil fuels. Flash photolysis of parent compounds forms the free radicals and resonance fluorescence or absorption is used to monitor their concentrations for rate coefficient measurements. The range of this technique was extended in this work to permit measurements from room temperature to practical combustion temperatures (ca. 1500°C). Rate coefficient measurements completed on the reaction $\text{O} + \text{CH}_4$ over the 125° to 1330°C range provide the first continuous data set available in this regime and give the following expression: $k = (2.63 \pm 0.55) \times 10^{-18} T^{2.36 \pm 0.03} \exp(-(3730 \pm 40)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The reaction of OH with C_6H_6 was investigated in the 400° to 700°C range; further study of this requires modifications to the apparatus and will be resumed when these are completed. Kinetic measurements on the reactions of CH_3 with O_2 and O are now in progress.

Chemical Physics, continued

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

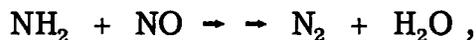
263. REACTIONS OF IONS WITH ATOMIC AND MOLECULAR FREE RADICALS \$52,000 01-02
W. Ronald Gentry
Department of Chemistry

In the reactions between two atomic or molecular species in which both species have open-shell electronic configurations, there will usually be several closely-spaced electronic potential energy surfaces for the system. Transitions among these surfaces may play an important role in the reaction dynamics. The University of Minnesota merged molecular beam facility is unique in its capability for measuring microscopic reaction cross-sections for such systems, over the range of relative kinetic energy from 0.001 eV to 30 eV. Recently completed work includes investigations of the reactions $H_2^+ + X \rightarrow XH^+ + H$, where $X = C, N, O, F$. The influence of the atomic quadrupole moment at very low kinetic energies permits the reaction probability to be determined as a function of angular momentum projection quantum numbers. Systems presently being studied include the reactions $X^+(XH^+) + YH(Y) \rightarrow XY^+ + H$, where $X, Y = C, N, O, F$.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

264. REACTION MECHANISMS IN COMBUSTION: FORMATION OF SOOT AND POLYCYCLIC AROMATIC HYDROCARBONS \$60,000 01-02
William A. Goddard, III
Department of Chemistry

We are studying the microscopic mechanisms of the gas phase and heterogeneous processes involved in the formation of soot and polycyclic aromatic hydrocarbons (PAH). The initial emphasis is on the mechanisms of formation of precursors to the soot nuclei. Later we will examine the homogeneous and heterogeneous processes (polymerization, chemisorption onto the soot nucleus, and dehydrogenation) involved in the growth of the soot nuclei and the formation of PAH. In carrying out these studies, we use ab initio theoretical methods including electron correlation (generalized valence bond, configuration interaction) to calculate detailed potential surfaces for the various reaction pathways. We have also examined the reaction mechanism for



presumed to be the critical step in the thermal DeNO_x process for converting NO to N₂ in stationary power plants.

Chemical Physics, continued

UNIVERSITY OF ILLINOIS/CHICAGO CIRCLE
Chicago, Illinois 60680

265. MEASUREMENTS OF GAS PHASE REACTION	\$53,000	01-02
RATES: $D+H_x$ AND $NO+O_3$	15 mo.	
Robert J. Gordon	FY 80-81	
Department of Chemistry		

In the first part of this study a flash-photolysis resonance-fluorescence apparatus was used to measure the rate constants of the reactions $H + HCl$, $Cl + H_2$ and $Cl + D_2$, over the temperature range 200-500 K. The ratio of the first two rate constants is in excellent agreement with detailed balance, thereby resolving a long-standing controversy. The ratio of the last two rate constants is in good agreement above 250 K with previous indirect measurements. In the second part of the study the chemiluminescent reaction of ozone with nitric oxide, and the vibrational relaxation of ozone by various scattering partners, are being studied. It was found that in the relaxation of O_3 by H_2O and D_2O complex formation rather than resonant energy transfer is responsible for the inverse temperature dependence of the rate constant.

BROWN UNIVERSITY
Providence, Rhode Island 02912

266. INTERACTIONS OF MOLECULES WITH SURFACES	\$64,000	01-02
E. F. Greene		
Department of Chemistry		

The interaction of molecules with surfaces is being studied in three kinds of experiments. First, measurements of the angular distribution of rare gas atoms, such as Ar and Kr, scattered elastically from crystalline surfaces is used to probe the structure of the outermost layer of the surface. Second, the efficiency with which atoms are ionized in collisions with surfaces is being studied to determine the work function of the surface and to learn about the nature of the electron transfer process. The cleanliness of the surface is checked using Auger spectra. Beams of atoms such as the alkalis and Tl are directed at surfaces of metals, semiconductors and insulators and the ion yield determined as the temperature of the surface is varied. Third, the abrupt transfer of kinetic to internal energy resulting from the impact of fast molecules on a stationary surface is being used to initiate chemical reactions. This activation by impact for the case of $W(CO)_6$ hitting a glass surface leads to the breaking of chemical bonds only at kinetic energies above a threshold of about 500 kJ mol^{-1} .

Chemical Physics, continued

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

267. THE STUDY OF COMBUSTION AND FLAME PROCESSES INITIATED BY IR LASER-INDUCED ABSORPTION \$65,000 01-02
William A. Guillory
Department of Chemistry

The phenomenon of infrared multiple-photon absorption, subsequently leading to excited and ground state dissociation products, simulates non-equilibrium processes occurring in flames and other combustion systems. Using visible and UV 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 efficiency of production, via IR n-photon dissociation, of CH and OH with oxidants (O₂, NO, etc.) are being studied as a function of CH vibrational excitation. Also being studied are the reactions of OH with NO and aliphatic and aromatic hydrocarbons. New techniques, such as multi-photon absorption fluorescence, are being implemented to study amounts and energy states of reactive and product species (CH₂, CH₃, CO, etc.). Discrete level and quasicontinuum energy transfer and relaxation in propynal, glyoxal and biacetyl are being studied.

ILLINOIS INSTITUTE OF TECHNOLOGY
Chicago, Illinois 60616

268. STUDIES OF COMBUSTION KINETICS AND MECHANISMS \$82,000 01-02
David Gutman
Department of Chemistry

The purpose of this research is to gain a more thorough and more basic understanding of hydrocarbon combustion mechanisms through obtaining an increased knowledge of the reactivity and role of polyatomic free radicals which are involved in gaseous combustion. A new versatile technique to generate polyatomic free radicals has been coupled with a sensitive method of monitoring their concentrations. Radicals are generated by the infrared multi-photon-induced decomposition of suitable precursors, and photoionization mass spectrometry is used to monitor their concentrations during the reaction with other molecules present in the system. Reactions of allyl radicals, generated by laser-induced decomposition of allyl bromide, with nitrogen dioxide and bromine are being studied. Details of their mechanisms and their rate constants are being obtained. Suitable free radical precursors are being tested as sources of methyl, ethyl, vinyl and acetyl radicals for future kinetic studies.

Chemical Physics, continued

STANFORD UNIVERSITY
Stanford, California 94305

269. COMBUSTION GAS MEASUREMENTS USING TUNABLE LASER ABSORPTION SPECTROSCOPY \$63,000 01-02
R. K. Hanson
Department of Mechanical Engineering

Objectives of this research are: (1) the measurement of fundamental spectroscopic parameters (band strengths and collision widths) for critical combustion species, particularly pollutants and radicals; and (2) the development of tunable laser absorption spectroscopy as a technique for species concentration measurements in combustion flows. Laser sources include a tunable CW infrared diode laser, a tunable CW ring dye laser, and a grating tunable waveguide CO₂ laser. Current experiments include band strength and collision-broadened linewidth measurements of HCN, NH₃, CO 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.

STANFORD UNIVERSITY
Stanford, California 94305

270. THE KINETICS OF SOME REACTIONS OF HCN AT HIGH TEMPERATURES \$59,000 01-02
R. K. Hanson and C. T. Bowman
Department of Mechanical Engineering

The objective of this research program is the determination of the mechanisms and rate parameters of several HCN decomposition reactions at high temperatures. A shock tube is used to heat various gas mixtures containing HCN, and spectroscopic diagnostics are employed to monitor time-histories of important species during reaction. Reactions of particular interest include the thermal decomposition of HCN and the reactions of HCN with H and O.

Chemical Physics, continued

HOWARD UNIVERSITY

Washington, District of Columbia 20059

271. LASER STUDIES OF THE DYNAMICS OF ATOM-
MOLECULE REACTIONS \$47,000 01-02
William M. Jackson
Department of Chemistry

This program is designed to measure the dynamics of atom molecule reactions using a tunable dye laser to determine the quantum state distribution of the reactive fragments. Presently, the exothermic reactions of carbon atoms are being studied. These atoms are produced by the VUV photolysis of carbon suboxide in the presence of a reactive diatomic or triatomic molecule. The laser probe is synchronized in time with the light source that produces the carbon atom so that at the proper delays the nascent distributions of the reaction intermediates can be determined. Work has also begun on coupling eximer lasers to molecular beams so that reactions between reacted species can be observed. A molecular beam apparatus that can be used to determine dark fragments that are produced as a result of chemical reactions has been built. An eximer laser is being used to produce reactive intermediates so that exothermic reactions that occur between these reactive intermediates may be investigated.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

272. HIGH-RESOLUTION INFRARED SPECTROSCOPY:
DISCRETE STATES IN THE QUASI-CONTINUUM \$60,000 01-02
Kenneth C. Janda
Division of Chemistry and Chemical
Engineering

High-resolution infrared spectroscopy of vibrationally excited states is used as a direct probe of intramolecular vibrational energy redistribution. Molecules under study are precooled in a supersonic nozzle expansion to greatly simplify spectroscopy. Transitions are observed from the ground vibrational and rotational levels directly to states embedded in the quasi-continuum. Any unique spectral features can then be related to dynamics of the excited state since the initial state does not contribute to spectral congestion. Two general types of experiments are performed. In the first type the photodissociation spectra of van der Waals molecules containing ethylene are studied. The dependence of predissociation rate on molecular structure, exit channel effects and vibrational excitation energy are determined. In the second type of experiment infrared fluorescence is used to detect spectra of vibrationally excited stable molecules. These experiments yield spectral features in exquisite detail (one part per ten million resolution) which can be related to intramolecular dynamics.

Chemical Physics, continued

STATE UNIVERSITY OF NEW YORK/STONY BROOK
Stony Brook, New York 11794

273. MULTIPHOTON DISSOCIATION SPECTROSCOPY AND PHOTOCHEMISTRY \$52,000 01-02
Philip M. Johnson
Department of Chemistry

This research is developing techniques for the study of the decomposition of molecules resulting from the multiphoton transitions induced by intense light fields. The yield of a given photofragment with respect to the wavelength of the light causing photodissociation is measured by using multiphoton ionization or fluorescence to detect the photoproduct. This produces a multiphoton dissociation spectrum which provides information about the relative decomposition pathways and the vibronic structure of excited states which decompose. These spectra are valuable and complementary supplements to multiphoton ionization spectra for the understanding of excited molecular states. Absolute photochemical rates are determined by use of the kinetic framework of multiphoton ionization. The technique is being initially used on oxygen molecules because of its simplicity and importance in the propagation of high intensity laser light through air. Other oxygen and hydrogen containing compounds will be studied and the technique extended to the detection of many molecular fragments, many of which are important in combustion processes.

UNIVERSITY OF NEW ORLEANS
New Orleans, Louisiana 70122

274. IDENTIFICATION AND TEMPORAL BEHAVIOR OF RADICAL INTERMEDIATES FORMED DURING THE COMBUSTION AND PYROLYSIS OF GASEOUS FUELS; KINETIC PATHWAYS TO SOOT FORMATION \$50,000 01-02
Ralph D. Kern, Jr.
Department of Chemistry

Synthetic fuels derived from coal or oil shale contain an abundance of aromatic compounds which are known to form copious amounts of soot during combustion. The chemical mechanism by which aromatic molecules are converted to soot is not known. Toluene is a major component in synthetic fuels and unleaded gasoline and this research program is studying the decomposition of toluene by recording the time history of compounds and radicals appearing in the reflected shock zone with a time-of-flight mass spectrometer. The primary goals are to develop product profiles, attempt to model the profiles using available rate constants, and determine the magnitude of the soot yield. The major products observed are acetylene and diacetylene which are stable in the range of 1800-2500 K. This finding coupled with mass balance results supports a low figure for soot conversion (<10%) and a mechanism which is composed mainly ring rupture steps resulting in low molecular compounds. The information obtained from this work will be useful in the design of efficient combustion devices and the control of undesirable exhaust compounds and particles.

Chemical Physics, continued

UNIVERSITY OF ILLINOIS/CHICAGO CIRCLE
Chicago, Illinois 60680

275. LASER SCHLIEREN, SHOCK TUBE STUDIES OF HIGH TEMPERATURE HYDROCARBON PYROLYSIS RATES \$55,400 01-02
John H. Kiefer
Department of Energy Engineering

The purpose of this project is the determination of rate constants for elementary reactions occurring in fuel hydrocarbon pyrolysis. Reactions of propane, ethylene, ethane, and butane, as well as aromatics, are being investigated. The technique is a combination of the shock tube with laser-schlieren measurement of the density gradient generated by endo or exothermic reaction. Although the pyrolysis of such fuels is complex, the direct access to rate afforded by this technique, together with its very high resolution, often allows a temporal separation of the mechanism into primary and secondary processes. Rates of initial fuel dissociation can then be determined to very high temperatures, and, by using various fuel mixtures, the rate for a number of important secondary reactions can also be measured to previously inaccessible temperatures.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

276. DEPOPULATION RATES FOR COMBUSTION-RELATED SPECIES IN LONG-LIVED VIBRATIONALLY OR ELECTRONICALLY EXCITED LEVELS \$100,000 01-02
James L. Kinsey and Robert W. Field
Department of Chemistry

In this research program a new technique, Stimulated Emission Pumping (SEP), will be used to investigate the properties of vibrationally hot electronic ground state and electronic metastable levels of a number of small molecules such as HCCH, H₂ CO, NO₂, CH₃O and HNO. The initial phases of this work are concentrating on the demonstration of SEP for preparing molecules in such states with complete rovibronic selectivity but without the usual limitations imposed by vibrational and electronic selection rules. This is to be followed by laser-induced-fluorescence (LIF) probing of the unimolecular and bimolecular decay rates of the prepared levels.

Chemical Physics, continued

THE JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

277. IONIC ASPECTS OF SOOT FORMATION	\$60,000	01-02
Walter S. Koski	16 mo.	
Department of Chemistry	FY81-82	

Studies of hydrocarbon flames indicate that ions play an important role in the process of soot formation. There is, however, a dearth of knowledge of the pertinent ion-chemistry and this research program is designed to correct this deficiency. Significant elementary ion-molecule reactions will be studied and these results will be correlated with reported combustion results. Ion beam techniques and tandem mass spectrometers will be used in these measurements. Ion-molecule reactions of $C_3H_3^+$, CHO^+ , H_3O^+ , etc. with acetylene, ethylene and benzene will be studied as a function of projectile ion kinetic energy. Cross sections will be measured and angular distributions of the product ions will be determined when necessary. Since charge transfer and proton transfer reactions involving aromatic products in the flame are believed to contribute to soot formation, such processes between light ions and aromatics as benzene and naphthalene will also be investigated.

STATE UNIVERSITY OF NEW YORK/BUFFALO
Amherst, New York 14226

278. MULTIPHOTON INTERACTIONS IN MOLECULES WITH PICOSECOND LASER PULSES	\$60,000	01-02
H. S. Kwok		
Electrical Engineering Department		

Ultrashort CO_2 laser pulses are employed in this program to study the process of infrared laser induced multiphoton interactions in polyatomic molecules. Variable duration pulses from 150 nsec to 30 psec are used. The high intensities in the ultrashort pulses precludes the rate equation description of the multiphoton process. Instead, a coherent interaction picture has to be used. It is because of the very large Rabi precession frequency obtainable at the ultrahigh intensities. Experimentally it is observed that the energy fluence scaling law, thought to be valid for the multiphoton process, is violated by these ultrashort pulses. At the same energy fluences, a 30 psec pulse is able to deposit 40 times more energy into a SF_6 molecule than an ordinary 100 nsec TEA laser pulse. This "superexcitation" process affords many interesting and useful possibilities such as mode-selective chemical reactions. The latter is possible because of a competition between up-pumping of the molecule and intramolecular energy transfer. Nonstatistical reaction kinetics behavior will be looked for at ultrahigh laser intensities.

Chemical Physics, continued

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

279. MEASUREMENT OF RADICAL SPECIES CONCENTRATIONS IN FLAMES BY FLUORESCENCE AND ABSORPTION USING A TUNABLE DYE LASER \$82,100 01-02
N. M. Laurendeau and D. W. Sweeney
School of Mechanical Engineering

The goal is to develop a saturated fluorescence technique which will yield accurate molecular number densities over a wide range of flame pressure, temperature and composition. A Nd:YAG-pumped dye laser producing a ten nanosecond pulse is used to excite an isolated rotational transition in the OH $A^2\Sigma^+-X^2\Pi$ electronic system. The resulting fluorescence is resolved both spectrally and temporally. Total OH number densities are calculated by collecting fluorescence from the directly excited upper rotational level, and using the balanced cross-rate model to analyze the experimental data. The OH number density agrees to within a factor of three with the results of independent OH absorption measurements. Significantly, the fluorescence/absorption number density ratio is nearly the same in 30, 100, and 250 torr $H_2/O_2/N_2$ flat flames, demonstrating the insensitivity of the fluorescence signal to the quenching environment of the radical. Rotational transfer rates are calculated by comparing the time development of the OH fluorescence spectrum with computer simulations.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

280. THEORETICAL STUDIES ON HETEROGENEOUS COMBUSTION \$46,000 01-02
Chung K. Law
Department of Mechanical and Nuclear Engineering

This program aims at gaining fundamental understanding on the basic physical and chemical mechanisms governing the vaporization, ignition, combustion, and extinction of fuel droplets and sprays in environments simulating those within practical combustors. During the reporting period we have extended the classical theory describing vaporization and combustion of droplets of pure fuel to the case of multicomponent fuel blends. Explicit expressions are derived allowing a priori assessment of the droplet burning rate. The theory agrees well with experimental results and is expected to be particularly useful for synthetic liquid fuels which suffer greater multicomponent effects. The effect of buoyancy on droplet combustion and extinction has also been studied. Explicit expressions for the burning rate and extinction criteria are derived.

Chemical Physics, continued

KANSAS STATE UNIVERSITY
Manhattan, Kansas 66506

283. DIFFUSION FLAME STUDIES OF THE CHEMICAL AND PHYSICAL MECHANISMS OF SOOT FORMATION FROM AROMATIC FUELS \$53,000 01-02
T. W. Lester, J. F. Merklin and C. M. Sorensen
Departments of Nuclear Engineering and Physics

This research program is designed to study the chemical and the physical mechanisms of soot formation from aromatic and substituted aromatic hydrocarbons. Our intent is to determine if ring stability is important in the formation of soot and if the chemical mechanism is free radical or molecular. We are using an opposed jet diffusion flame supported either by carbon monoxide or hydrogen. The fuel side is doped with a known concentration of either benzene, substituted aromatic, or mixtures of the aromatic hydrocarbon with an aliphatic hydrocarbon. Sampling for stable species is being done with a microquartz probe and the samples are being analyzed by gas chromatography and mass spectrometry. Photon correlation spectroscopy is being used to map the soot number density and size distribution as a function of position in the flame and temperature.

UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

284. EXPERIMENTAL STUDIES OF THE IONIZATIONS AND BONDING OF SMALL MOLECULES ATTACHED TO TRANSITION METALS \$62,000 01-02
Dennis L. Lichtenberger
Department of Chemistry

One objective of the present work is to obtain experimental information relating to the electronic interactions between metals and small molecules in structurally characterized complexes. The primary approach being developed is the high-resolution electron spectroscopy (XPS and UPS of gases) of small molecules attached to metals in organometallic complexes. The recently developed ability to observe metal-ligand vibrational fine structure in the ionizations is contributing in a unique and major way to an understanding of the interactions in these systems. Small molecules receiving attention include carbonyl, thiocarbonyl, nitrosyl, thionitrosyl, sulfur dioxide, olefins, methylene, and others. The different bonding modes of these molecules are being studied in various mononuclear and dinuclear complexes. The systems are directly associated with recent developments in organometallic synthesis and catalysis.

Chemical Physics, continued

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

285. LASER INDUCED CHEMICAL REACTIONS AND
LASER-COLLISION PROCESSES \$60,000 01-02
John C. Light
James Franck Institute and
Department of Chemistry

The photodissociation of triatomic molecules may produce fragments which are excited electronically, vibrationally, or rotationally. The excitation pattern is affected by the initial state, the photon energy, the Franck-Condon factors, and the scattering processes as the fragments fly apart. We are trying to model this process accurately using quantum scattering techniques for both symmetric (CO_2) and asymmetric (HCN) triatomic molecules. We use an R-matrix propagation method for the scattering, and accumulate overlap integrals during the scattering calculation. For collinear CO_2 , Fano type resonances and vibrational structure are seen in the cross sections as functions of $h\nu$. We are also determining the multiphoton absorption probability and dissociation probability for model diatomic molecules in very strong laser fields by a time independent, non-perturbative L^2 technique. Very sharp multiphoton resonances are observed on a model problem and the response of HF is now under study.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

286. ELECTRONIC RELAXATION PROCESSES IN \$59,000 01-02
POLYATOMIC MOLECULES
Edward C. Lim
Department of Chemistry

The overall goal of this research is to gain better understanding of the mechanism of electronic relaxation in molecules of importance to photochemistry, photobiology and energy conversion processes. The molecular systems that are being investigated are nitrogen-heterocyclic and aromatic carbonyl compounds which exhibit unusually efficient nonradiative decays and composite molecules (charge-transfer complexes, exciplexes and excimers), whose nonradiative decay characteristics are poorly understood. The effects of temperature and solvent (polarity and viscosity) on excited (singlet) state dynamics of these compounds are being probed by time-resolved fluorescence spectra and energy-resolved fluorescence decay, following picosecond excitation by a synchronously-pumped dye laser. The spin sublevel dynamics of the lowest triplet state of a few of these compounds are also being studied by optical detection of magnetic resonance for the purpose of deducing detailed mechanisms of intersystem crossing processes.

Chemical Physics, continued

UNIVERSITY OF KANSAS
Lawrence, Kansas 66045

287. STEREOELECTRONIC PROPERTIES OF AGGREGATED CHLOROPHYLL SYSTEMS \$79,100 01-02
Gerald M. Maggiora
Departments of Chemistry and
Biochemistry

This project seeks, through the use of quantum mechanical and other theoretical techniques, to elucidate the electronic factors which contribute to photosynthetic energy conversion. Earlier studies were directed towards characterization of electronic structural features such as transition energies, oscillator strengths, and polarizations of chlorophyll and related photosynthetic pigments. Current studies are directed towards more complex dimer and trimer pigment systems. Recently completed empirical potential function calculations have provided a number of insights into the geometric structure of "stacked" porphyrin and "special-pair" chlorophyll dimers, and the electronic structure studies are being extended to these systems in an effort to gain new insights into the nature of their excited electronic states. In addition, a quadratic valence force field is being developed in order to characterize the electronic ground and excited state vibrational properties of the photosynthetic pigments. This information will be used to interpret the IR and Resonance Raman spectra of these pigments and, coupled with electronic structural information, to characterize their photodynamic properties.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

288. MOLECULAR BEAM STUDIES OF METASTABLE RARE GAS CHEMILUMINESCENT REACTIONS \$50,000 01-02
11 mo.
Richard M. Martin
Department of Chemistry

Metastable rare gas chemiluminescent reactions are being studied using a crossed molecular beam optical spectrometer to obtain emission spectra and a crossed molecular beam time-of-flight spectrometer to obtain cross sections as a function of collision energy. The major objectives of this research program are to determine reaction cross sections and product state distributions as a function of collision energy, and compare these results with theoretical reaction models in order to elucidate the reaction mechanisms. The collisional processes under study include neutral excitation reactions, fluorescent chemionization reactions, and atom transfer reactions giving excited rare gas halide and oxide molecules. The information to be obtained in this work is of current interest in furthering knowledge of excited state chemistry, and is also of practical importance for understanding the fundamental dynamic processes which occur in excited rare gas reaction systems such as rare gas excimer and excitation transfer lasers.

Chemical Physics, continued

PRINCETON UNIVERSITY
Princeton, New Jersey 08544

289. DYNAMICAL STUDIES OF MOLECULAR SYSTEMS \$78,000 01-02
Herschel Rabitz
Department of Chemistry

Three specific avenues of study are being pursued: (a) studies of critical parameter dependencies in chemical kinetics and collision dynamics, (b) the development and application of scaling relations between collision cross sections, and (c) the study of new integral equation techniques for the practical treatment of the Schrödinger equation in collision dynamics. The research in category (a) involves the further development and implementation of new sensitivity analysis techniques to ascertain the key molecular parameters controlling collision behavior and chemical kinetics. Part (b) of the research aims to provide a simplifying framework for the analysis of collisional relaxation measurements by means of identifying the reduced set of fundamental cross sections. Finally, part (c) of the research is connected with the derivation and application of a new practical collision dynamical procedure for reducing the original partial differential Schrödinger equation into an effective ordinary differential equation without coupled channel techniques. All aspects of the research are being applied to realistic kinetic and collisional systems.

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

290. A KINETIC STUDY OF RADICAL-AROMATIC \$54,000 01-02
HYDROCARBON REACTIONS
A. R. Ravishankara
Engineering Experiment Station

Chemical kinetic and mechanistic investigations of free radical-aromatic hydrocarbon reactions of importance to optimization of energy-production from alternative fuel sources are being pursued. Improvement in the fundamental understanding of the rates and pathways characteristics of these gas-phase reactions is the principal objective of this program. Specifically, using the technique of (laser/spark discharge) flash photolysis-(resonance/laser induced) fluorescence, absolute rate constant measurements for the oxidation chain step reactions $O(OH,H) + \text{aromatic hydrocarbons}$ are being made as functions of temperature and, when appropriate, pressure. Particular reaction pathways in the above processes are being probed either via measurements of reaction product concentration-time profiles or through the application of kinetic isotope effect theory to rate constant measurements on isotopically substituted analogs of the above reactions. Information gained from these studies is expected to facilitate improved utilization of aromatic hydrocarbons both as combustibles and as feedstocks for production of substitutable synthetic fuels, as well as further basic understanding of aromatic hydrocarbon reactions.

Chemical Physics, continued

CALSPAN CORPORATION/ADVANCED TECHNOLOGY CENTER
Buffalo, New York 14225

291. VIBRATIONAL ENERGY TRANSFER KINETICS IN MOLECULAR DISEQUILIBRIUM \$59,911 01-02
J. William Rich
Aerodynamic Research Department

In these experiments, a continuous wave carbon monoxide laser is used to excite the vibrational mode of carbon monoxide in mixtures of CO and various additive gases flowing through an absorption cell. The nonequilibrium conditions created in the cell result in the substantial population of very high lying vibrational quantum states (to $V = 42$) of CO, although the gas kinetic temperature remains near 300 K. Under these conditions, the carbon monoxide reacts to form vapor phase C_2 and CO_2 ; carbon suboxide (C_3O_2) polymer is deposited on the cell walls. The C_2 and C_3O_2 products have been determined to be isotopically enriched in ^{13}C . The details of the kinetic mechanism of these reactions have been determined. Isotope separation results have been compared with recent theoretical studies of enrichment by vibration-vibration pumping. Experiments are in progress to determine if the products are also enriched in ^{18}O , as predicted by theory.

STANFORD UNIVERSITY
Stanford, California 94305

292. EFFICIENCY OF THERMAL AND CHEMICAL ENGINES \$78,000 01-02
John Ross
Department of Chemistry

This research is concerned with the efficiency of thermal and chemical engines. Power production necessitates irreversible processes with corresponding dissipation. The presence of such processes requires investigation of engine cycles for specified performance criteria. Optimal control theory is one approach and is being applied to thermal engines with inertial properties. Energy transduction in oscillatory chemical reactions has the possibility of variable dissipation and efficiency. This process is being investigated in glycolysis in which the chemical intermediates oscillate in time. The effect of external noise on such systems is being investigated.

Chemical Physics, continued

UNIVERSITY OF CALIFORNIA/BERKELEY
Berkeley, California 94720

293. SPECTROSCOPY AND STRUCTURES OF REACTIVE INTERMEDIATES IN FLAMES WITH FAR-INFRARED LASERS \$80,000 01-02
Richard J. Saykally
Department of Chemistry

This research program is designed to provide spectra and structures of reactive intermediates generated in flames using extremely sensitive intracavity far-infrared laser absorption techniques. The molecules to be studied are important in the contexts of combustion mechanisms, soot formation, flame inhibition, and pollution; many have never been detected before by spectroscopic methods. Information extracted in these studies will include precise bond distances and angles, electronic structures, dipole moments, and collision cross-sections. The spectra, measured in situ, will probe species concentrations and temperatures in the flames.

WRIGHT STATE UNIVERSITY
Dayton, Ohio 45435

294. THE DIRECT DETERMINATION OF ATOM AND RADICAL CONCENTRATIONS IN THERMAL REACTIONS OF HYDROCARBONS AND OTHER GASES \$50,000 01-02
G. B. Skinner
Department of Chemistry

The general goal of this research is to study the kinetics of the atom and free radical reactions that are important in combustion reactions, by following the appearance and disappearance of H, O, OH and other such combustion intermediates. H and O atoms are currently being measured using resonance absorption measurements in the vacuum ultraviolet. Recently an extensive series of O measurements in H₂-O₂-Ar and D₂-O₂-Ar mixtures of widely varying stoichiometries has been completed, and also another series of O measurements in N₂O-H₂-Ar and N₂O-D₂-Ar mixtures, both of which lead to kinetic data for elementary reactions. C₃H₈-O₂-Ar and C₃D₈-Ar mixtures have also been studied within the past year.

Chemical Physics, continued

RICE UNIVERSITY
Houston, Texas 77001

295. HYPERSONIC BEAM LASER PHOTOLYSIS \$57,000 01-02
R. E. Smalley
Department of Chemistry

The objective of this research is to develop powerful new techniques for the detailed spectral study of free radicals, diradicals, and other reaction intermediates cooled to near absolute zero in a hypersonic beam. Two general approaches are being pursued. The first involves laser fragmentation of a suitable gas-phase precursor seeded in a hypersonic free jet of an inert gas carrier such as argon or helium. The second involves laser vaporization of a metal plug within a pulsed hypersonic nozzle. In either case the result is the production of an intense beam of highly reactive but cold and collision-free radicals. The structure and dynamics of these exotic species is then probed by laser-induced fluorescence, resonant two-photon ionization, or photofragment rejection. Specific cases under study include the organic radical benzyl (C_7H_7) and a variety of organometallic radicals of catalytic importance such as FeC and $FeCO$.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

296. LASER FLUORESCENCE STUDIES OF THE DETAILED \$60,000 01-02
COMBUSTION OF NITROGEN AND SULFUR BEARING
FUELS
M. Steinberg, K. Schofield, and D. O. Harris
Quantum Institute

The research program is designed to identify the chemistry important in the conversion of fuel nitrogen to NO_x , identify the nature of any interactions between NO_x and SO_x chemistries, and any effects of nitrogen and sulfur on CH and C_2 behavior in flames. Quantitative laser-fluorescence monitoring conditions developed for OH , SO , SO_2 , SH , S_2 , CS , and NH are being extended to NH_2 , CH , NO , NO_2 , C_2 , and CH . The time varying absolute concentration profiles of these species above the burner are monitored in series of fuel-rich, atmospheric pressure, $H_2/O_2/N_2$ and C_2H_2/N_2 flames with temperatures ranging from 1700 to 2500 K and containing up to 1% sulfur and fuel nitrogen dopants. The measured species profiles are analyzed in terms of rapid bimolecular radical reactions which can account for the production and coupling of the radical intermediates and the slower recombination processes which lead to stable products. Effort is also being directed toward completing our understanding of the SO_x cycle in the hydrogen and hydrocarbon flame systems.

Chemical Physics, continued

UNIVERSITY OF CALIFORNIA/SAN DIEGO
La Jolla, California 92093

297. SHOCK-TUBE STUDIES OF IMPORTANT COMBUSTION-REACTION STEPS INVOLVING METHYL RADICALS Klaus G. P. Sulzmann Energy Center	\$55,000 16 mo. FY80-81	01-02
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The goal of this study is to unravel the fate and the detailed kinetics of the methyl radical as an important intermediate during the combustion of hydrocarbons by investigating its pyrolysis as well as its chemical interactions with O₂, O, H, OH, etc. The methyl radicals are produced behind reflected shock-waves in argon-diluted mixtures containing (CH₃)₂CO₂ as a donor at temperatures between 1500 and 2500°K and at total pressures between 1 and 2 atm. Absolute intensity-time histories are obtained by absorption spectroscopy for CH₃, O, H, CH₂ and CH₃O, as well as by infrared emission techniques for CO₂ and H₂CO. The results are used to define important elementary reaction paths governing the fate of CH₃. Computer analysis is employed in order to construct reaction models and determine rate coefficients which account for the observed concentration-time histories and to identify dominant reaction steps which are of importance to hydrocarbon combustion systems.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

298. VARIATIONAL TRANSITION STATE THEORY Donald G. Truhlar Department of Chemistry	\$105,000 24 mo. FY 81-82	01-02
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This research involves the development, testing, and implementation of new theoretical methods for calculating the rate coefficients of chemical reactions from potential energy surfaces. The methods are also used to calibrate semiempirical potential energy surfaces against experiment. Particular emphasis is placed on combustion reactions and kinetic isotope effects. Current efforts are directed primarily to extending the formalism to reactions of polyatomic species, to improving the treatment of tunneling in systems with highly curved reaction paths, and to the proper treatment of anharmonicity. The reaction OH + H₂ → H₂O + H is being studied as a prototype system for testing new methods.

Chemical Physics, continued

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

299. KINETIC DATA BASE FOR COMBUSTION MODELING Wing Tsang and R. F. Hampson Chemical Kinetics Division	\$80,000	01-02
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The fundamental goal of this program is to construct an evaluated chemical kinetic data base for the detailed modeling of hydrocarbon combustion processes. Initial work involves the collection of recommended rate data and all subsequent experimental work. Present work is concerned with all reactions pertinent to methane pyrolysis and oxidation. This will be followed by tables dealing with NOX formation and the pyrolysis and oxidation of higher aliphatics. Data evaluation is carried out by experienced kineticists making full use of the facilities of the Chemical Kinetics Information Center, an arm of the National Standard Reference Data System.

DYNAMICS TECHNOLOGY, INC.
Torrance, California 90505

300. COMPUTATION OF TURBULENT REACTING FLOWS: COMPARISON OF VARIOUS MIXING/CHEMISTRY INTERACTION MODELS John J. Wormeck	\$78,942	01-02
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This research program is an analytical and computational study to compare various mixing/chemistry interaction models for turbulent combustion. Both equilibrium and finite-rate chemistry are utilized. Emphasis is directed towards a probability density function (PDF) approach. A novel technique has been developed in which the turbulent-chemistry correlations are modeled by PDF and then solved by a finite-difference procedure. Such a technique has the potential of describing both micro- and macro-mixing required in turbulent combustion. In all of these combustion simulations, a detailed fully coupled two-dimensional fluid flow scheme is employed. All of the results are being compared to experiment.

Chemical Physics, continued

STANFORD UNIVERSITY
Stanford, California 94305

301. INTERNAL ENERGY DISTRIBUTION OF THE PARENT MOLECULE AND ITS PHOTOFRAGMENTS FOLLOWING IR MULTIPHOTON ABSORPTION
Richard N. Zare
Department of Chemistry

\$60,000 01-02

Infrared multiple photon absorption and dissociation of molecules is studied through the time resolved internal energy distributions of the photofragments. Dissociation of acrylonitrile by a pulsed CO₂ TEA laser produces the C₂(a³Π_u) and CN(2Σ⁺) molecules. Fragment rotational state distributions are probed during the laser pulse by Laser Induced Fluorescence spectroscopy and fit by a Boltzmann distribution to give rotational temperatures (T_R). The effect of the laser pulse shape and energy on T_R is determined by selectively removing the "tail" of the pulse with a plasma shutter. The effect of single mode excitation on T_R is determined by modification of the laser cavity, through the addition of apertures and a low pressure gain cell, to provide single mode operation. This details the roles of laser intensity and pulse energy in the absorption process. These results are compared to theoretical predictions based on possible absorption and dissociation mechanisms. Dissociation of other parent molecules is under investigation in order to find theoretically more tractable systems.

Atomic Physics

NEW YORK UNIVERSITY
New York, New York 10003

302. ENERGY-RELATED ATOMIC AND MOLECULAR STRUCTURE AND SCATTERING STUDIES \$80,000 01-03
Benjamin Bederson
Department of Physics

Two experimental programs are in progress: atomic and molecular structure studies, and low-energy scattering of electrons by highly polar molecules. We have completed a series of measurements of the average dc electric dipole polarizabilities of a number of alkali halide dimers: $(\text{CsCl})_2$, $(\text{RbCl})_2$, $(\text{KCl})_2$, $(\text{CsF})_2$, and $(\text{KF})_2$, and have compared to suitably modelled bond and ionic polarizabilities, with reasonable success. Some high-Z atomic systems are now being studied, in particular Bi and U (as well as In), using state-selection in order to obtain tensor components of the polarizability. In the scattering work, a new type of high-current electron monochromator employing a cylindrical electron beam has been constructed. It is capable of delivering up to 10^{-6} A, for recoil-type scattering experiments. A new beams apparatus 5 meters long, with high angular and energy resolution, is being used in order to resolve forward scattering ($1-5^\circ$ in the polar scattering angle), which dominates scattering in highly polar systems. A single-mode cw tunable ring-laser has been acquired to extend such studies to excited states.

THE UNIVERSITY OF NEW MEXICO
Albuquerque, New Mexico 87131

303. ATOMIC PHYSICS WITH RELATIVISTIC BEAMS \$88,000 01-03
Howard C. Bryant
Department of Physics and Astronomy

The resonance structure of the H^- ion is being probed with laser beams and static electromagnetic fields at the 800 MeV linear accelerator at LAMPF (Los Alamos National Laboratory). The large relativistic effects present in the transformation from the laboratory to the barycentric frame of the ion, which is traveling at 0.842 the speed of light, allow the effective production of photon energies and electric field strengths well beyond the capability of standard laboratory techniques. The single photon photoejection of both electrons from the H^- , leaving an H^+ , is being studied with the center-of-mass photon energies ranging up to 15.8 eV. The cross section is being measured for the two electron photoejection process, which is of fundamental importance to the understanding of the atomic 3 body problem, as a function of photon energy and electric field. The absolute energy of the ^1P Feshbach resonance near $n=2$ is being determined. A pulsed magnet, capable of applying magnetic fields up to 30 KG, is under construction for use in studies of the behavior of H^- resonances in the presence of very strong motional electric fields.

Atomic Physics, continued

COLLEGE OF WILLIAM AND MARY
Williamsburg, Virginia 23185

304. NEGATIVE ION DETACHMENT CROSS SECTIONS \$64,772 01-03
R. L. Champion and L. D. Doverspike
Department of Physics

The objectives of this research program are to investigate the collisional dynamics for a variety of reactants involving atomic negative ions and molecular targets. The experiments consist of both absolute total- and doubly-differential cross section measurements. The energy range of the experiments is from several eV up to a few hundred eV. Negative ions which are being studied include H^- , D^- , O^- and various halogen negative ions. The processes under investigation are collisional detachment, collisional excitation by negative ions, and reactive scattering. Careful analyses of the effects of isotopic substitution (H^-/D^-) coupled with the cross section measurements provide a basis upon which to calculate rate constants, test proposed collisional models and potential surface calculations, and to understand the chemical pathways of negative ions in various environments.

UNIVERSITY OF KANSAS
Lawrence, Kansas 66045

305. MANY-BODY PROCESSES IN ATOMIC AND MOLECULAR PHYSICS \$45,000 01-03
Shih-I Chu
Department of Chemistry

The fundamental goals of this project are to develop nonperturbative quasi-energy methods for investigating atomic and molecular processes in intense fields. (1) A complex quasi-vibrational energy method has been developed for studying molecular photodissociation, using only square-integrable (L^2) functions. By means of the complex coordinate transformation and L^2 - discretization of the vibrational continua, the complex quasi-vibrational energies of the Floquet Hamiltonian can be determined, the real parts of which provide the A. C. Stark-shifted vibronic energies, whereas the imaginary parts are related to photodissociation rates. The theory is applied to the direct photodissociation of H_2^+ ($1s\sigma_g - 2p\sigma_u$) in both weak and strong fields. (2) A procedure has been developed for extending the method of complex coordinate to numerical potentials and any arbitrary analytical potentials. This method, together with the complex coordinate - coupled channel formalism developed in our laboratory, is being extended to the study of multi-channel rotational predissociation of Ar- N_2 van der Waals molecules.

Atomic Physics, continued

UNIVERSITY OF TOLEDO
Toledo, Ohio 43606

306. SEMI-EMPIRICAL STUDIES OF ATOMIC STRUCTURE	\$50,000 24 mo. FY80-81	01-03
Larry J. Curtis Department of Physics and Astronomy		

A program of semi-empirical studies of the properties of the very heavy and very highly ionized atomic systems which often occur as contaminants in controlled fusion devices is being carried out. The high precision requirements for spectroscopic analysis of these systems can exceed the capabilities of present ab initio theoretical methods, but semi-empirical approaches have been found which provide very accurate predictions. Empirical model parametrizations of existing data have revealed unexpected linearities which have been exploited to make extensive predictions along isoelectronic and homologous sequences. These empirical regularities also provide insight into the theoretical approximations which can be applied to these extremely relativistic atomic systems. Experimental measurements of the semi-empirical predictions are carried as part of the program, both to test the methods and to enlarge the data base.

HARVARD-SMITHSONIAN CENTER FOR ASTROPHYSICS
Cambridge, Massachusetts 02138

307. THEORETICAL STUDIES OF HIGHLY IONIZED SPECIES	\$78,650	01-03
A. Dalgarno		

In an ionized plasma containing only a small fraction of neutral species charge transfer recombination significantly modifies the ionic composition. The process has specific end products which may reveal their existence by the emission of radiation. The radiation is a potentially valuable diagnostic probe of the physical conditions in the plasma and may yield information on the ion temperature. Detailed calculations have been carried out of the emission lines resulting from a range of atomic systems that are present or could be injected into the plasma. Limited experimental data are available at intermediate energies and methods have been developed which will enable the extension of the present low energy calculations to higher energies. Non-thermal ions are produced by the dissociative ionization of molecules by a mechanism involving excitation into intermediate autoionizing Rydberg states. A quantitative description of the mechanism for molecular hydrogen has been worked. The modifications of the properties of heavy atoms due to relativistic effects have been explored.

Atomic Physics, continued

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

308. BASIC STUDIES OF ATOMIC DYNAMICS	95,000	01-03
U. Fano		
Department of Physics		

This continuing project aims at identifying mechanisms that control the correlated motions of particles in collisions and photoprocesses and the resulting transfers of energy between different motions. Electron motions were earlier at the center of attention but molecular vibrations and collisions are now added to them. To this end a unified framework has been developed which encompasses all processes and centers on the evolution of a transient complex from its condensation limit to a fragmentation limit. Earlier descriptions of the correlated motion of an electron pair in the field of an ionic core with central symmetry have now been extended to the field of an open-shell core which can exchange angular momentum and energy with the outer pair; the specific example treated is the complex $\text{He}^{-**} = \text{He}^+ + (2e)$. The theory of Rydberg electrons in a Stark field has been readied for realistic applications through a twin development: a) an accurate semi-analytic treatment applicable to atomic H, and b) a semi-analytic treatment of the modifications required when the ion H^+ is replaced by a multi-particle ion.

VANDERBILT UNIVERSITY
Nashville, Tennessee 37235

309. THEORETICAL STUDIES OF ATOMIC TRANSITIONS	\$59,230	01-03
Charlotte Froese Fischer		
Computer Science Department		

The present research is part of an ongoing project in atomic structure calculations using the MCHF method. The primary emphasis is on correlation effects. Relativistic effects are estimated using an intermediate coupling type calculation based on a Breit-Pauli approximation. The program for computing allowed transition probabilities has been extended to include forbidden transitions of interest in plasma diagnostics. An integrated set of programs, capable of executing interactively on minicomputers, is being developed in collaboration with A. Hibbert and D. Ridder. Several transitions of current interest have been investigated. These include a study of lifetime trends in the Mg sequence, the forbidden $2s^2 2p^4 \ ^1S - 2s^2 2p^4 \ ^1D$ transition in oxygen and transitions to doubly excited states in Be II. The study of lifetime trends was undertaken with a view towards identifying important cascade contributions in beam-foil spectroscopy of the Mg sequence. Be II is a relatively simple system and as such is a suitable test case for the study of calculations for excited states.

Atomic Physics, continued

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

310. FREE CHARGED PARTICLE BEHAVIOR IN INTENSE LASER FIELDS David M. Fradkin Department of Physics	\$29,000 24 mo. FY80-81	01-03
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This project involves a theoretical study of the asymptotic effects produced by an intense laser pulse interacting with an otherwise free charged particle that may also be subjected to auxiliary electromagnetic fields. Classical as well as quantum-mechanical models of the interaction are being analyzed in order to provide insight into the mechanisms of energy-momentum transfer from the fields to the particle, and to establish the functional dependence of such transfer on pulse energy, laser polarization, etc. Possible asymptotic spin polarization change of the charged particle is being studied, in the classical realm, by employing the coupled Bargmann-Michel-Telegdi equations for inhomogeneous fields (modified to incorporate radiation reaction), and in the quantum-mechanical realm, by means of the Dirac equation with a Pauli term to include the effect of an anomalous magnetic moment of the particle. The intense laser pulse is included in the zero-order solution by appropriate resolution on a null-plane coordinate basis.

SRI INTERNATIONAL
Menlo Park, California 94025

311. STUDIES OF AUTOIONIZING STATES RELEVANT TO DIELECTRONIC RECOMBINATION Thomas F. Gallagher Molecular Physics Laboratory	\$61,204	01-03
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The goal of this program is to reach a thorough understanding of autoionization of alkaline earth atoms and the effects of perturbations such as electric fields upon the autoionization. Multistep tunable laser excitation of alkaline earth atoms in an atomic beam is used to excite the autoionizing states allowing very precise spectroscopic measurements, both with and without external electric fields. In addition a high resolution electron energy analyzer is used to determine the final states resulting from autoionization. The results of the experiments are compared with theoretical models.

Atomic Physics, continued

UNIVERSITY OF OKLAHOMA
Norman, Oklahoma 73019

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| 312. EXPERIMENTAL AND THEORETICAL STUDY OF
VERY LOW INELASTIC PROCESSES IN ELECTRON-
MOLECULAR COLLISIONS | \$100,000 | 01-03 |
| D. E. Golden and M. A. Morrison | | |
| Department of Physics and Astronomy | | |

This research program entails comprehensive theoretical and experimental studies of very-low-energy electron-impact excitation of molecules in an effort to determine reliable cross sections for a variety of collision problems of basic scientific interest and relevance to technological applications such as advanced energy programs. This work seeks to resolve numerous significant discrepancies between various determinations of near-threshold electron-impact excitations of molecules and to develop a deeper understanding of the physics of these important collision processes. To attain these goals, absolute differential cross sections for this process will be measured using a newly-designed crossed-beam time-of-flight apparatus and a new molecular beam source. The results will be compared with those determined by accurate ab-initio calculations. The theoretical studies entail development of methods to treat exchange and polarization effects in the sensitive near-threshold region and of techniques for coping with the breakdown of the adiabatic-nuclei theory. The initial joint effort is in e-H₂ scattering, but in the future e-N₂, e-CO, and e-CO₂ scattering will be considered.

LOUISIANA STATE UNIVERSITY
Baton Rouge, Louisiana 70803

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| 313. ELECTRON COLLISIONS WITH POSITIVE IONS | \$92,500 | 01-03 |
| Ronald J. W. Henry | | |
| Department of Physics and Astronomy | | |
| | 24 mo. | |
| | FY81-82 | |

The fundamental goals of this project are to delineate the important physical processes which govern electron impact excitation processes for highly stripped 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 excitation of $2\ell-3\ell^1$ in Li-like C³⁺, O⁵⁺, Ne⁷⁺, Ar¹⁵⁺, and Fe²³⁺. Isoelectronic trends are being investigated so as to obtain information on ions of Cr, Fe, Ni, and Ti. Inner shell excitation cross sections are being calculated for Na-like Al²⁺ and Si³⁺, since this process after autoionization contributes significantly to total ionization cross sections.

Atomic Physics, continued

THE UNIVERSITY OF TEXAS
Austin, Texas 78712

314. KINETIC STUDIES FOLLOWING STATE SELECTIVE LASER EXCITATION	\$125,000	01-03
J. W. Keto	24 mo.	
Department of Physics	FY81-82	

In this project, electron energy transfer from excited states of xenon atoms and excimers is being studied. These states are produced selectively using multiphoton laser excitation. Their reaction rates with other molecules or atoms are measured in a flowing cell by measuring the time decay of their fluorescence. Similarly, energy disposal into product states is analysed by their fluorescence or by probing their populations using laser induced fluorescence. Initial experiments have been studying quenching of $5p^56p$ xenon atomic states in collisions with xenon and other rare gases. High resolution two-photon excitation spectra are being used to obtain accurate potential curves for the xenon dimer and excimers. Studies of energy disposal in molecular reactants are initially emphasizing chlorides.

OREGON STATE UNIVERSITY
Corvallis, Oregon 97331

315. THERMAL-ENERGY SCATTERING OF ATOMS IN HIGH RYDBERG STATES	\$45,407	01-03
Carl A. Kocher		
Department of Physics		

Collision processes are investigated for thermal-energy encounters between long-lived highly excited Rydberg states and ground-state gaseous targets. Previous measurements in our laboratory have demonstrated that high-Rydberg atoms are deflected in collisions with atomic and molecular targets. Excited states in an atomic beam are detected by field ionization, with velocities resolved by a time-of-flight technique using an on-line computer. The scattered Rydberg atoms are recorded as a function of scattering angle after the primary beam has passed through a localized target region. Because of the large average radius for the Rydberg valence electron, the electron and the core ion tend to scatter independently. The valence electron provides a charge-neutralizing sheath surrounding the core ion, rendering its trajectory virtually unaffected by non-ionizing external fields. Since ion-beam scattering experiments have heretofore proven difficult at thermal energies, this research program seeks to develop and exploit a new method for the determination of velocity-resolved free-ion cross sections.

Atomic Physics, continued

UNIVERSITY OF MISSOURI/ST. LOUIS
St. Louis, Missouri 63121

318. LOW ENERGY ION-NEUTRAL COLLISIONS \$62,000 01-03
J. J. Leventhal
Department of Physics

This experimental program is directed toward obtaining detailed information on energy transfer processes in atomic and molecular interactions. These energy transfer processes involve the intraconversion of kinetic and internal energies. The partitioning of internal energy among the available quantum states of the products of these inelastic processes is diagnosed primarily by dispersal and detection of radiation from the decay of these excited products. By examining changes in these spectra as a function of the relative kinetic energy of the colliding species information on the intraconversion of kinetic and internal energies is obtained. Recent work has centered on ion/atom or atom/atom collisions involving one or more laser excited reactants. These studies are yielding valuable information on the possibility of "laser switching" of atomic and molecular reactions.

UNIVERSITY OF ARKANSAS
Fayetteville, Arkansas 72701

319. A THEORETICAL STUDY OF ELECTRON CAPTURE \$36,659 01-03
IN ION-ION AND ION-ATOM COLLISIONS
M. Lieber and F. T. Chan
Department of Physics

Electron capture processes in ion-atom and ion-ion collisions, e.g. $A^+ + B \rightarrow A + B^+$, are of great intrinsic interest as well as importance to several areas of research, such as the controlled fusion energy program, astrophysics, and atmospheric phenomena. As a prototype of a rearrangement collision which is experimentally accessible, charge exchange has been studied since the earliest days of quantum mechanics, but the difficulty of calculation has limited theoretical progress. Recent work has shown that eikonal techniques can be successfully applied to problems of this type, and have surprising power and simplicity. Calculations are being performed on: (A) Electron capture from He^+ in collisions with fast protons and multicharged ions; (B) Electron capture from atomic hydrogen by fast C^{+6} , O^{+8} and Fe^{+24} projectiles (three ions of significance in magnetically confined fusion plasmas); (C) Electron capture from multielectron atoms by fast bare nuclei; (D) Differential cross sections in fast ion-atom collisions.

Atomic Physics, continued

KANSAS STATE UNIVERSITY
 Manhattan, Kansas 66506

320. ATOMIC PHYSICS OF STRONGLY CORRELATED SYSTEMS \$65,000 01-03
 Chii-Dong Lin
 Department of Physics

The goal of this project is to identify the dynamics of the correlated motion of atomic particles and the mechanism of subsequent breakup processes. This study is fundamental to the development of a comprehensive theory of inelastic atomic transitions in collisions with photons, electrons and heavy ions. Current efforts are along two directions: (1) the visualization and mapping of the correlated motion of two doubly-excited electrons in hyperspherical coordinates. Applications to H^- and He and to Li^- and Be atoms have revealed the advantages of the new approach; (2) the appropriate dynamical collision model for charge transfer in ion-atom collisions at medium velocities. We have shown that the dynamic model based on the extended two-center atomic expansion method using eigenstates of the separated atoms and of the united atom with plane-wave translational factors also can be extended to the lower collision energy region.

NATIONAL BUREAU OF STANDARDS
 Boulder, Colorado 80303

321. ATOMIC AND MOLECULAR COLLISION PROCESSES \$84,000 01-03
 David W. Norcross
 Quantum Physics Division

This program is focused on processes involved in diagnostics and modeling of fusion and MHD plasmas. An extensive series of calculations of cross sections and excitation rates for electron-induced transitions involving the ground and $n=2$ states of nine helium-like ions has been completed. These included the effect of series of autoionizing resonances converging on the $n=2$ and $n=3$ states, which were found to often enhance the excitation rates by significant factors. Work is in progress to assess the effect of these new rates on plasma diagnostics. A new technique for approximating the exchange interaction in electron-molecule collisions has been demonstrated, as well as the efficiency and flexibility that judicious use of the unitarized Born approximation can bring to collision calculations. A method has been developed that permits the full power of the adiabatic-nuclei approximation (normally applicable to non-polar molecules only) to be brought to bear on electron collisions with polar molecules. A very simple technique has been devised for the calculation of energy-loss and stopping cross sections employing this method.

Atomic Physics, continued

UNIVERSITY OF ROCHESTER
Rochester, New York 14627

322. NONLINEAR OPTICS WITH BROAD-BAND LASERS \$53,250 01-03
Michael G. Raymer
The Institute of Optics

Experiments are being carried out to study the effects of laser bandwidths in several important nonlinear optical processes. A nonlinear cross-correlator, based on parametric sum-frequency generation, is being developed and used to make novel measurements of the correlations which develop between pump and probe waves in stimulated Raman scattering, in both the amplifier and generator configurations. Pulsed dye lasers with independently variable bandwidths are used as pump and probe sources. The experiments, done in hydrogen gas, have been planned such that dispersive effects, which tend to destroy the correlations, are negligible. Also, experiments are being performed which probe the effects of laser bandwidth in multiphoton ionization, by generalizing the technique of nonlinear auto-correlation to include the detection of atomic ions in a two-photon ionizable cesium vapor.

KANSAS STATE UNIVERSITY
Manhattan, Kansas 66506

323. ATOMIC PHYSICS WITH HIGHLY IONIZED IONS \$425,000 01-03
Patrick Richard
Department of Physics

This research program is directed toward the study of the interaction of highly charged ions with neutral atoms. Interactions at medium and high ion velocities are performed with beams from the Kansas State University tandem accelerator. Interactions at very low velocities are being studied using the recoil ion source method developed at Kansas State. At the medium and high velocities the total and differential cross sections for single and double K-shell to K-shell charge transfer are being investigated by observing the projectile charge state dependence of the yield of K x-ray/Auger satellites and hypersatellites, respectively. At the very low velocities, single and multiple electron capture and transfer ionization processes have been identified by a double recoil method (the target and projectile charge states, before and after the collision, are determined) for Ar^{+q} with He, Ne, Ar and Xe at projectile energies between 250 and 660 eV per charge. Interactions leading to target alignment in the L shell are also being studied by observing the angular distribution of the emitted L x rays from the target.

Atomic Physics, continued

UNIVERSITY OF TENNESSEE
Knoxville, Tennessee 37916

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| 324. DIFFERENTIAL CHARGE TRANSFER TO THE
CONTINUUM BY IONS IN ATOMIC HYDROGEN
I. A. Sellin and S. B. Elston
Department of Physics | \$45,000 | 01-03 |
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Studies of the velocity spectrum and yield of electrons captured to the continuum by bare nuclei traversing atomic hydrogen targets are under way. In particular, measurements for 1 MeV/u bare carbon nuclei are being attempted. Such measurements are expected to greatly aid evaluation of different theoretical predictions of the size and shape of the differential cross section. To avoid problematic stray magnetic fields generated by large heating currents in most atomic hydrogen oven designs, an electron impact-heated oven has been designed, fabricated, and tested. Steady operation at temperatures above 2400° K has been achieved. Measurements of dissociation fractions by monitoring coincident bound-state capture vs. temperature are being attempted.

UNIVERSITY OF NORTH CAROLINA
Chapel Hill, North Carolina 27514

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| 325. EXPERIMENTAL STUDIES OF ATOMIC INNER
SHELL IONIZATION PHENOMENA
S. M. Shafroth
Department of Physics and Astronomy | \$56,000 | 01-03 |
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This research program is designed to study atomic inner shell vacancy production. The TUNL FN tandem Van de Graaff and sputter ion source are being used to produce bunched and chopped as well as D.C. beams of heavy ions so that metastable and prompt x-ray and Auger electron emitting ions can be studied. Thickness effects with solid targets on H.I. induced x ray production are being studied to find the probability for ejecting two K electrons from a Cl^{9+} projectile as a function of projectile energy. Radiative electron capture (R.E.C.) by projectiles with K-shell vacancies in solid targets vs. target thickness and atomic number (Z) and projectile energy and ionization state are underway. Preparations are being made to use synchrotron to produce vacancies near the threshold for K electron ejection to study Resonant Raman Auger electron spectra. Studies of the inverse Auger effect with quasi-free electrons are in progress. The relationship of this process to energy-loss processes in fusion reactors is being investigated.

Atomic Physics, continued

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

326. NEAR-RESONANT ABSORPTION BY ATOMS IN INTENSE FLUCTUATING FIELDS \$48,500 01-03
Stephen J. Smith
Joint Institute for Laboratory Astrophysics

This research is directed to measurement of photon absorption by atoms immersed in very intense laser radiation fields, when the radiation is in near-resonance with an atomic transition. A primary objective is to compare the behavior of an atom immersed in a monochromatic field with the behavior in a field on which statistical fluctuations are imposed. An optical double resonance technique is used to measure absorption to the $3P_{3/2}$ level and the broadening, shifting and splitting of the $3P_{3/2}$ ($F = 3$, $M_F = +3$) level in optically pumped atomic sodium, as a function of laser intensity, frequency detuning, and fluctuation parameters. Original concepts are incorporated in a ring laser and electronic control system with a demonstrated line-width capability of less than 100 kHz and a power output of about one watt. Absorption characteristics are analyzed on the axis of an unfocused Gaussian single mode beam from this laser at an intersection with a collimated atomic beam. Field fluctuations are imposed with an acousto-optic modulator driven by an appropriate frequency-modulated radio-frequency signal.

WRIGHT STATE UNIVERSITY
Dayton, Ohio 45435

327. ENDOTHERMIC NEGATIVE ION-NEUTRAL REACTIONS \$85,000 01-03
Thomas O. Tiernan and Richard L. C. Wu
Department of Chemistry

The objectives of this research program are to measure excitation functions and energy thresholds for certain charge-transfer and collision-induced dissociation (CID) reactions of FeO^- , FeO_2^- , PO_2^- and AlO_2^- , which are potentially important in various high-temperature environments. These data yield bond dissociation energies and heats of formation of these ions, as well as electron affinities of the corresponding neutral molecules. These measurements are made with a tandem mass spectrometer. Concurrently, detailed differential scattering measurements are being accomplished with a crossed ion-molecular beam apparatus for the endothermic reactions, $\text{O}^-/\text{D}_2 \rightarrow \text{OD}^-/\text{D}$; $\text{Br}^-/\text{Br}_2 \rightarrow \text{Br}_2^-/\text{Br}$; $\text{O}_3^-/\text{Ar} \rightarrow \text{O}^-/\text{O}_2$, Ar; as well as similar reactions of FeO_2^- . These studies will yield details of the kinematics and energy partitioning of such processes, and will improve the accuracy of thermochemical data derived from ionic reaction threshold measurements. In addition, these results will enhance our understanding of the microscopic mechanisms of endothermic ion-neutral reactions, and the energy surfaces on which these processes occur.

Atomic Physics, continued

RICE UNIVERSITY
Houston, Texas 77001

328. ENERGETICS OF ATOMIC AND MOLECULAR INTERACTIONS \$165,000 01-03
G. K. Walters and N. F. Lane
Department of Physics

This program emphasizes studies of structure and interactions of excited atoms, molecules, electrons and ions. Research areas include reactions and radiative lifetimes in atomic and molecular systems of high-efficiency laser promise, spin dependence in electron-atom scattering and understanding of spectra and collisional effects of interest in plasma physics and controlled thermonuclear reaction technology. Specifically, time resolved spectroscopy of alkali-halide excimers excited by synchrotron radiation is yielding stimulated emission cross-sections, formation and quenching rates for excimer laser transitions. A new method for measuring electron exchange and cooling rates in electron-atom/molecule collisions has been developed. New theoretical results include cross sections for: radiative charge-transfer collisions between He^{++} ions and H atoms; inelastic electron-ion collisions in a dense, hot plasma; energy transfer in collisions of highly excited atoms with molecules.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

329. X-RAY EMISSION IN HEAVY ION COLLISIONS \$55,479 01-03
R. L. Watson
Department of Chemistry

High resolution x-ray spectroscopy is being used to study the distributions of inner-shell vacancy states produced in projectile and target systems as a result of high energy heavy ion collisions. The elucidation of chemical and environmental influences on the numerous excited states leading to x-ray emission is of particular interest. Measurements are being performed on a variety of solid and gaseous fluorine compounds to investigate the mechanisms for inter-atomic electron transfer. The effects of dynamic screening and collision broadening on the energies, widths, and polarizations of x-rays emitted from highly stripped ions moving in solids are being examined using 2 MeV/amu beams of Ne, Mg, and S. ions.

Atomic Physics, continued

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

330. DETERMINATION OF SELECTED ATOMIC DATA PERTINENT TO ENERGY RELATED RESEARCH A. W. Weiss and W. L. Wiese Atomic and Plasma Radiation Division	\$100,000	01-03
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The objective of this research project is to produce selected, high quality data on atomic processes pertinent to energy related research. The project has two major components, 1) a basic research effort in atomic structure theory, and 2) a program of critical evaluation and compilation of atomic transition probability data. The theoretical work is directed toward a study of approximation methods for atomic structure calculations where relativistic corrections and electron correlation are both important. Pilot calculations, utilizing non-relativistic correlation information to correct relativistic calculations, are being done for highly stripped ions of iron. The data evaluation work is concentrating on transition probabilities for the elements Sc through Ni. The compilation of iron, cobalt and nickel is in press, and the earlier compilations of Sc through Mn are being updated and reevaluated for the purpose of producing a comprehensive compilation of critically evaluated data on all the transition metal elements in all stages of ionization.

Chemical Energy

YALE UNIVERSITY
New Haven, Connecticut 06511

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| 331. STUDIES OF THE HYDROGENATION OF SMALL
UNSATURATED MOLECULES USING ORGANOMETALLIC
CLUSTER COMPOUNDS AS CATALYSTS
Richard D. Adams
Department of Chemistry | \$125,000
24 mo.
FY81-82 | 02-01 |
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The reactivity of transition metal cluster hydride compounds toward small heteronuclear unsaturated molecules is being investigated. It is believed that these compounds may form the basis for a new class of homogeneous hydrogenation catalysts. Research is being focused on the nature of the activation of CO, CO₂ and related molecules at polynuclear metal centers. The mechanisms of hydrogen transfer from the metal atoms to these substrates is of principal interest. The structure and bonding of partially hydrogenated substrates which remain coordinated to the clusters is being studied by infrared, nuclear magnetic resonance, and x-ray crystallographic analyses. Efforts to produce catalytic cycles based on cluster compounds are being carried out.

UNIVERSITY OF NORTH CAROLINA
Chapel Hill, North Carolina 27514

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| 332. THE HEATS OF FORMATION OF GAS PHASE
ORGANOSULFUR MOLECULES, RADICALS AND IONS
MEASURED BY PIPECO
Tomas Baer and Slayton A. Evans, Jr.
Department of Chemistry | \$65,000 | 02-01 |
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The structures and energies of organo-sulfur neutral radicals and ions are being investigated by photoionization mass spectrometry. The goal of the research is to learn about the chemistry and stability of transient sulfur containing species which may play a role in the sulfur emission from coal combustion. Molecules of particular interest are synthesized by novel synthetic routes. These molecules are photoionized and various fragment ions are collected as a function of the photon energy. Fragment ion appearance energies (AE) are then related to the heats of formation of the unknown species by the thermochemical cycle $AE = \Delta H_f^\circ(\text{ion fragment}) + \Delta H_f^\circ(\text{neutral fragment}) - \Delta H_f^\circ(\text{parent neutral})$. This equation is only correct in the special case when the dissociation is fast in comparison with the ion collection time and there is no reverse activation barrier. The former can be determined by measuring the decay rate while the latter can be estimated from the measured kinetic energy release. Both of these properties are measured by photoion-photoelectron coincidence.

Chemical Energy, continued

BRIGHAM YOUNG UNIVERSITY
Provo, Utah 84602

333. COBALT SUPPORT INTERACTIONS IN CO HYDROGENATION \$60,000 02-01
Calvin H. Bartholomew
Department of Chemical Engineering

This investigation focuses on cobalt and to a lesser extent iron metal-support interactions and their effects upon adsorption, electronic, and activity selectivity properties of these metals. Oxidation states and dispersions of cobalt are being determined as a function of metal loading and support by means of ESCA, temperature programmed reduction, and H₂ and CO adsorption. Activity/selectivity properties of the same cobalt catalysts for CO hydrogenation are being studied with a single pass, differential laboratory reactor. Binding energies and binding states of CO and H₂ on cobalt catalysts are measured using temperature programmed desorption. The electronic and magnetic properties of iron on different supports are under investigation using Mossbauer spectroscopy.

WEBER STATE COLLEGE
Ogden, Utah 84408

334. THE ROLE OF THE HYDROGEN-DONOR SOLVENT IN COAL HYDROLIQUEFACTION \$55,000 02-01
15 mo.
Robert R. Beishline
Department of Chemistry

The objective of this research is to determine the nature of the intrasolvent hydrogen transfer reactions in which 1,2-dihydronaphthalene (1,2-DHN) and its dihydrophenanthrene analogues participate concurrently with the solvent-coal hydrogen transfer reactions during coal hydrogenation. The gas phase kinetics of disproportionation of 1,2-DHN into tetralin, naphthalene and dimers (380-420°C) are consistent with either a free radical or a carbonium ion mechanism. Some of the dimers produced by the free radical mechanism, however, have different structures than those produced by the carbonium ion mechanism. The dimers are therefore being isolated by preparative GC, and their structures investigated using mass spectroscopy and NMR. Molecular hydrogen is also produced in the thermolysis of 1,2-DHN. The quantitative amount of hydrogen produced is being measured as a function of temperature. Preliminary liquid phase kinetics for the thermolysis of 1,2-DHN (280-320°C) have been obtained, and refinements on the experimental procedure are being worked out.

Chemical Energy, continued

PURDUE UNIVERSITY
W. Lafayette, Indiana 47907

335. REDUCTION OF AROMATIC COMPOUNDS DERIVED FROM COAL BY CALCIUM Robert A. Benkeser Department of Chemistry	\$65,000 16 mo. FY81-82	02-01
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This research program is designed to apply two new reducing systems recently discovered in this Laboratory to aromatic organic compounds obtainable from coal tar. These new methods employ calcium metal dissolved in mixed amine solvents or in liquid ammonia to which small amounts of hexamethylphosphoric triamide (HMPA) have been added. These new reductions should provide economical routes to cyclic olefins presently not available and which could prove very useful as chemical intermediates. The reduction of compounds derivable from coal tar are under active investigation. These include the xylenes, indene, α - and β -methylnaphthalenes, biphenyl, acenaphthalene, fluorene etc. The feasibility of an electrolytic reduction of these compounds is also under investigation. The experimental procedure used in these reductions is patterned after that developed for the now well established lithium-amine reducing system. There is reason to believe that the calcium reagents will be more selective than the lithium system, especially in the case of hindered hydrocarbons.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

336. ACTIVATION AND RECOVERY OF HOMOGENEOUS CATALYSTS USING POLYMERS David E. Bergbreiter Department of Chemistry	\$34,000	02-01
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These research studies are designed to explore the ways in which readily available functionalized polymers can be used to improve or enhance the efficiency and utility of homogeneous catalysts. Acceleration of the rate of homogeneous hydrogenation reactions is being studied initially and can be accomplished by selectively removing non-volatile catalyst inhibitors or poisons using metal polystyrene sulfonates. Selectivity in such processes is the result of diffusional limitations commonly associated with crosslinked polystyrene networks which discriminates against reaction of larger catalyst complexes with the polymeric reagents. Polymers designed to absorb or entrap a homogeneous catalyst are also being studied. Catalysts bound to noncrosslinked polymers can be dissolved at elevated temperatures so as to form homogeneous solutions in which catalysis can occur. Cooling or addition of a poorer solvent produces a filterable precipitate polymer which encapsulates the catalyst complex. Catalysts bound to these non-crosslinked polymers are characterized by FT NMR.

Chemical Energy, continued

STANFORD UNIVERSITY
Stanford, California 94305

337. CATALYTIC STEAM GASIFICATION OF CARBON	\$83,844	02-01
Michel Boudart	28 mo.	
Department of Chemical Engineering	FY80-81	

Our goal is to understand the role of metal in the platinum-catalyzed gasification of carbon by water vapor, carbon dioxide and hydrogen. Kinetics under differential and integral conditions determines the reaction orders, activation energies, product selectivities and kinetic isotope effects. In the reaction between carbon and hydrogen, the metal-carbon interaction has been found to be more important than the metal-gas or carbon-gas interaction. Changing rates, total surface areas and platinum surface areas are currently being measured as the carbon is gasified by hydrogen. Physical adsorption of nitrogen and hydrogen adsorption provide a measure of total and platinum surface areas, respectively. Finally, controlled atmosphere electron microscopy is being used to study in situ the interaction between palladium and carbon during the gasification by carbon dioxide of graphite and amorphous carbon.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

338. AN INTEGRATED APPROACH TO THE SYSTEMATIC SYNTHESIS, CHARACTERIZATION, AND CATALYTIC ACTIVITY OF NOVEL HETEROGENEOUS CATALYSTS	\$124,520	02-01
Alan Brenner	24 mo.	
Department of Chemistry	FY80-81	

This research program has been involved in the development of a new class of catalysts consisting of carbonyl complexes directly bonded to inorganic oxide supports. Using an integrated approach to catalysis, the new technique of temperature programmed decomposition has been combined with a series of model reactions to yield a structure-activity relationship. This relationship allows for the a priori prediction of the method of synthesis to yield the most active catalyst as well as a prediction of when the new catalyst is likely to be more active than traditional catalysts. Using this systematic approach to synthesis, about twenty catalysts have been developed which are at least ten fold more active than their traditional counterparts. Some base metals which were previously believed to have very low activity have now been found to mimic some of the more expensive noble metals and might be able to replace them for certain reactions. Preliminary tests using Fischer-Tropsch synthesis and hydrodesulfurization, reactions of immediate interest to the chemical industry, have also shown improved performance in some cases.

Chemical Energy, continued

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

339. THE PROPERTIES OF SUPPORTED METAL CATALYSTS R. L. Burwell, Jr., J. B. Butt and J. B. Cohen Ipatieff Laboratory	\$180,000 22 mo. FY81-82	02-01
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The objectives of this project are to examine the properties of supported metal catalysts via systematic characterization of morphological and geometric properties combined with chemical studies of specific chemisorption and catalytic probe reactions. Studies have now encompassed graded series of Pt/SiO₂, Pt/Al₂O₃, Pd/SiO₂, and are being extended to CoRh/SiO₂. Extensive controlled atmosphere x-ray characterization has been carried out and, most recently the hydrogenolysis of methylcyclopropane has been conducted in situ in the diffractometer. This has permitted for the first time the direct observation of the formation of Pd hydride on working catalysts under reaction conditions. Other chemical studies continue to investigate the effect of pretreatment conditions on the apparent structure sensitivity of hydrogenation, hydrogenolysis, and exchange reactions on these catalysts. Novel preparation methods are being used to prepare the CoRh series, with heteronuclear cluster carbonyls employed as impregnating agents. This should improve alloy homogeneity over what has been reported in the past.

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

340. MECHANISTIC STUDIES RELATED TO THE METAL CATALYZED HYDROGENATION OF CARBON MONOXIDE TO HYDROCARBONS Charles P. Casey Department of Chemistry	\$159,095 27 mo. FY80-81	02-01
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Transition metal compounds which are models for intermediates proposed in the metal catalyzed hydrogenation of carbon monoxide are being synthesized and their chemical reactions are being studied. Metal formyl compounds are prepared by borohydride reduction of metal carbonyl compounds. Detailed comparisons of metal formyl compounds (M-CO-H) with the better known metal acetyl compounds (M-CO-CH₃) are being carried out to determine the unique properties of metal formyl compounds. Comparisons of structures, kinetic stability, and thermodynamic stability are being done. It is crucial to know the thermodynamic stability of M-CO-H relative to M-H + CO to access whether metal formyl species (M-CO-H) are viable intermediates in CO reduction. Hydroxymethyl metal compounds (MCH₂OH) have also been prepared as models for intermediates in CO reduction. These compounds are being synthesized and their reactions with CO, H₂, acids, and bases are being studied. The synthesis and reaction of heterobimetallic compounds are being studied as potential new catalysts for CO reduction.

Chemical Energy, continued

INDIANA UNIVERSITY
Bloomington, Indiana 47405

341. TRANSITION METAL AND MIXED METAL ALKOXIDES AND OXIDES Malcolm H. Chisholm Department of Chemistry	\$115,000 24 mo. FY81-82	02-01
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This research program is exploring the analogy between metal oxides and metal alkoxides. A structural analogy has been established between the hydrocarbon soluble alkoxides $W_4(OEt)_{16}$, $Mo_4O_8(OPr-i)_4(py)_4$ and $[Ti(OEt)_4]_4$ and the oxides $Ag_8W_4O_{16}$ and the ternary metal oxides $Ba_{1.13}Mo_8O_{16}$: all contain M_4O_{16} units which are discrete in the alkoxides or repeating units in the polymeric oxides. The M_4O_{16} unit can accommodate cluster electrons varying in number from 0 through 12. The reactivity of the cluster alkoxides and the dinuclear alkoxides $M_2(OR)_6$, which contain metal-to-metal triple bonds, towards small unsaturated molecules such as CO, acetylenes and olefins is being investigated. Intriguing new adducts have been isolated and an olefin isomerization and an acetylene polymerization catalyst have been discovered. These new reactions may model reactivity patterns associated with heterogeneous metal oxide catalysts. The key role of the oxide systems is believed to involve (i) strong π -donation to the metal and (ii) strong metal-to-metal bonding.

WESLEYAN UNIVERSITY
Middletown, Connecticut 06457

342. HOMOGENEOUS CARBON MONOXIDE FIXATION Alan R. Cutler Department of Chemistry	\$115,000 24 mo. FY81-82	02-01
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Discrete organometallic complexes containing C_1 ligands formally derived from the reduction of terminally bound CO are being synthesized in order to delineate those coordinated ligand reactions and their intermediates that are viable for the hydrogenation of ligated CO. The C_p Fe, Mo and W carbonylate fragments serve as convenient vehicles for synthesizing stable η^1 -formyl, η^2 -formyl, C- and O-bound -formyl (bimetallic), and 2° -alkoxycarbene complexes. These complexes, represent plausible intermediates for forming initial C-H bonds during CO fixation, and permit examination of the role of Lewis acid complexation towards both stabilizing and activating the formyl ligand to further hydride addition. Conversion of alkoxymethyl complexes, obtained by reduction of cationic CO complexes of the above Fe, Mo, and W fragments, specifically to C_2 organic products via a sequence of coordinated ligand reactions is also under investigation.

Chemical Energy, continued

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

343. STUDIES OF NEW ELIMINATION REACTIONS OF METAL COMPLEXES \$26,560 02-01
Mary Rakowski DuBois
Department of Chemistry

This research program is investigating new elimination reactions which occur at organosulfur ligands in certain metal complexes. The work may prove important in understanding the reactions catalyzed by metal sulfide surfaces. In particular certain reduced derivatives of dimeric complexes of molybdenum of the type $[C_2H_5M(S)SR]_2$ (R=H or alkyl) have been found to eliminate alkanes or alkenes from the sulfur ligands while the M_2S_4 cores remain intact. Reduced complexes with various R substituents on the sulfur ligands are being isolated and mechanistic studies of the eliminative coupling reactions are being carried out. Other pathways for alkyl elimination reactions from sulfur ligands are also being studied. Thermally induced eliminations may proceed by homolytic S-C bond rupture, but dimeric complexes of this type may have alternate low energy pathways for decomposition, e.g., elimination of a hydrogen from a position α or β to the sulfur atom. The thermal decompositions of $[C_2H_5Mo(SCH_3)_2]_2$ and $[C_2H_5MoSC_2H_4S]_2$ may proceed by the latter pathways, and mechanistic studies are in progress.

ROCKWELL INTERNATIONAL
Canoga Park, California 91304

344. MOLTEN SALT INTERACTIONS IN COAL PROCESSING \$160,000 02-01
G. B. Dunks and S. J. Yosim
Energy Systems Group

The purpose of this project is to develop an understanding of the chemical and physical processes operating in the oxidation of carbon in molten salt media. Emphasis is placed on the in situ identification of the species present in sparged beds of molten sodium carbonate and the determination of the concentrations of these species under differing experimental conditions. Electrochemical methods are employed to study the changes which occur in the steady-state melt composition with respect to the melt temperature (900-1000 C) and the composition of the sparge gas. Sparge gas mixtures containing carbon monoxide, carbon dioxide, oxygen and nitrogen in various ratios are used. These results together with the results of parametric studies in which the composition of the exhaust gas from graphite oxidation experiments was determined, are used to identify the active intermediates in the oxidation of graphite in molten sodium carbonate. These studies are extended to include molten sodium sulfate and sodium carbonate-sodium sulfate mixtures.

Chemical Energy, continued

UNIVERSITY OF TEXAS
Austin, Texas 78712

345. STUDY OF FISCHER-TROPSCH SYNTHESIS THROUGH THE USE OF SURFACE INTERMEDIATE SCAVENGERS	\$117,100 36 mo. FY80-82	02-01
John G. Ekerdt Department of Chemical Engineering		

The goal of this program is to develop a more complete understanding of the reaction intermediates involved in Fischer-Tropsch synthesis. Studies are being carried out over oxide-supported metals, Fe, Ru and Ni, thought to exhibit a common reaction pathway, methylene addition to alkyl fragments, and at the same time a different product distribution. Insight into the surface reaction mechanism is gained by investigating the reactive characteristics of adsorbed hydrocarbon fragments. This is accomplished by scavenging the synthesis-generated fragments from the metal surface with a cyclic internal olefin, cyclohexene. The olefin reacts with surface fragments to form alkyl substituted cyclic products in which the alkyl group varies in carbon number. The substituted cyclic hydrocarbon distribution is related to the hydrocarbon distribution on the surface. Scavenged product dependence on synthesis conditions and catalyst composition will be used to develop reaction mechanisms, kinetic expressions, and a better understanding of synthesis selectivity.

COLORADO STATE UNIVERSITY
Ft. Collins, Colorado 80523

346. CHEMICALLY MODIFIED CARBON, PLATINUM AND NICKEL ELECTRODES	\$62,000 16 mo. FY81-82	02-01
C. M. Elliott Department of Chemistry		

This project, which is a continuation of efforts started at the University of Vermont, remains directed at the problem of catalyzing heterogeneous redox processes utilizing chemically modified electrodes. Several specific areas of investigation have been identified in our study. These areas are: (1) Preparation and investigation of surfaces modified with heterobimetal complexes consisting of ruthenium (II) and a second, different transition metal; (2) Preparation and investigation of modified surfaces having surface bound chelating ligands or chelate complexes; (3) Studies of the catalytic reduction of alkyl halides at iron porphyrin polymer modified electrodes; (4) Preparation of "electrode-bindable" complexes that incorporate two components of the photochemical water splitting reactions within one molecule; (5) Preparation and characterization of "viologen-like" polymer coated electrodes.

Chemical Energy, continued

UNIVERSITY OF VERMONT
Burlington, Vermont 05405

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| 347. CHEMICALLY MODIFIED CARBON, PLATINUM
AND NICKEL ELECTRODES
C. M. Elliott
Department of Chemistry | \$46,000
8 mo. | 02-01 |
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The goal of this project is to prepare new chemically modified electrode surfaces which may potentially alter the kinetics of various solution electrode reactions. Of primary interest is the catalysis of various kinetically inert small molecules that are of economic interest, in particular, the respective four electron and six electron reductions of dioxygen and dinitrogen. Different synthetic procedures appropriate for each of the materials under study are being investigated in order to chemically bind the potential catalyst to the surfaces of bulk carbon, platinum, and nickel. Concurrently, a number of novel metalloporphyrin compounds have been prepared and their catalytic activity is presently under investigation. Several types of electrode materials have now been modified by surface bound polymers containing electrochemically active material. The primary methods of investigation of these surfaces are electrochemical, including such techniques as chronoamperometry, cyclic voltammetry and the rotated disk electrode technique.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

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| 348. SYNTHESIS, CHEMISTRY AND CATALYTIC ACTIVITY OF LANTHANIDE METALS IN UNUSUAL OXIDATION STATES AND COORDINATION ENVIRONMENTS
William J. Evans
Department of Chemistry | \$60,000 | 02-01 |
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The objective of this investigation is to identify the special chemical properties of the lanthanide metals (a series of 14 heavy metals which are mined in California) which distinguish them from other metallic elements and to exploit this unique chemistry to develop new catalytic reactions which presently are not achievable with conventional catalysts. The basic chemistry of the lanthanide metal carbon bond is being determined by studying the reactions of tetra(alkyl)lanthanide complexes, R_4Ln^- , and bis(cyclopentadienyl)lanthanide alkyl complexes, $(C_5H_5)_2LnR$. The reaction of the latter class of molecules with hydrogen gas forms soluble lanthanide hydrides, whose catalytic chemistry is being studied for the first time. The alkyl complexes also react with carbon monoxide to form first an acyl complex which incorporates one molecule of CO and then a bimetallic enedione diolate complex in which 4 molecules of CO have been chemically connected in two, fused, 6-membered, metallocyclic rings. The catalytic chemistry and photochemistry of these products is also being studied.

Chemical Energy, continued

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

349. HOMOGENEOUS CATALYSIS OF THE WATER GAS SHIFT REACTION \$55,000 02-01
Peter C. Ford
Department of Chemistry

This research is concerned with the design and characterization of homogeneous catalysts for the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$). Major effort is being directed toward elucidating the fundamental chemistry of catalysts based on ruthenium and iridium carbonyl complexes in alkaline solution and on ruthenium carbonyl in acidic solution and found in this laboratory to be active for the shift reaction. Reaction kinetics are carried out using gas chromatography and major solution species are studied using in situ infrared, nuclear magnetic resonance and electronic spectroscopy. Mechanisms of model reactions considered key steps in probable catalysis cycles (e.g., $\text{Ru}(\text{CO})_5 + 2 \text{OH}^- = \text{HRu}(\text{CO})_4^- + \text{HCO}_3^-$) are also being studied by a combination of kinetics and spectroscopic techniques.

CORNELL UNIVERSITY
Ithaca, New York 14853

350. ESR STUDIES OF SURFACE ADSORPTION AND CATALYSIS UNDER ULTRA-HIGH VACUUM CONDITIONS \$70,000 02-01
Jack H. Freed
Department of Chemistry

The objective of this project is the development of a new approach for the study of surface adsorption and catalysis on clean metallic and oxide surfaces by ESR spectroscopy. While ESR has previously been extensively used in studies on insulator (in particular, oxide) surfaces, such studies usually suffer from the failings of either 1) not having a well-characterized surface and/or 2) not having ultra-high vacuum (UHV) conditions in order to guarantee that it is clean. In the experiments performed in this project, the microwave cavity is itself part of the UHV system, so that clean metallic surfaces are prepared by vacuum evaporation onto the interior of the cavity walls. Various clean gases are then directly adsorbed onto the surface and in situ ESR spectra are obtained which permit the study of paramagnetic adsorbates and surface reaction kinetics. These studies are complemented by simultaneous studies of the new phenomenon: CREMSSEE (cyclotron resonance from microwave stimulated secondary electron emissions), which is also observed in the UHV-ESR microwave cavity and is found to be very sensitive to bonding.

Chemical Energy, continued

INDIANA UNIVERSITY
Bloomington, Indiana 47405

351. RADICAL CHAIN AND REARRANGEMENT REACTIONS IN COAL LIQUEFACTION	\$115,000 24 mo. FY81-82	02-01
Joseph J. Gajewski and Kevin E. Gilbert Department of Chemistry		

This project focuses on providing fundamental data for the thermal reactions of aromatic hydrocarbons that will serve as a basis for understanding coal liquefaction processes. Specific areas of concern include radical chain processes, inhibition by phenols and aromatic amines, reactions of unstabilized radicals, unimolecular processes liberating CO₂ and olefins, and pericyclic reactions. Analysis of the kinetics and energetics of coal liquefaction suggests that radical chain processes are involved. The determination of the rates and chain lengths for model compounds such as 1,3-diphenylpropane and dibenzylether may establish the maximum contribution to be expected from these processes in coal liquefaction. Studies of the chain length in the presence of inhibitors such as phenols and aromatic amines will permit an evaluation of the amount of inhibition in coal liquefaction. Since radical chain processes represent the most efficient means of depolymerizing coal, mechanisms that slow down chain processes will be carefully investigated. Aromatic pericyclic reactions will be examined as well.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

352. MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION	\$50,000	02-01
Gregory L. Geoffroy Department of Chemistry		

Mechanistic schemes for the metal surface catalyzed reduction of carbon monoxide to methanol and to hydrocarbons have been proposed, and the feasibility of these mechanisms are being tested by preparing and studying the chemistry of metal clusters which resemble the proposed surface intermediates. Initial focus has been on the preparation and reactivity studies of cluster complexes bearing formyl and acyl substituent groups. The stepwise reduction of CO to CH₄ on an Os₃ cluster has been observed and experiments directed toward elucidating the mechanism of this conversion are being conducted. A series of mixed-metal dinuclear complexes have been synthesized and their CO/H₂ reactivity is being examined. Focus is on dinuclear complexes containing one early and one late transition metal and held together by bridging μ -PR₂ and μ -SR groups.

Chemical Energy, continued

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

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| 353. CONTRIBUTION OF CELLULOSE AND LIGNIN TO
THE ORIGIN OF THE VITRINITIC MACERALS OF
COALS | \$61,600
16 mo.
FY81-82 | 02-01 |
|---|-------------------------------|-------|
- Peter H. Given
Earth and Mineral Sciences

The objective of this program is to define more precisely the role of lignin and cellulose in contributing to coalification and to identify chemical structures in coals. Recent work using radioactive tracers suggests that the polysaccharides of plants are rapidly destroyed in peats, the precursors of coals. However, microscopic examination of thin sections of peats and of a lignite indicates that cellulose does survive to a significant extent. Perhaps the basic skeletal structures of plant polymers all form part of the input to coalification, but in a chemically altered form. To test this hypothesis, various investigative techniques are being applied to the humin fraction of four representative peats from the Florida Everglades, and also to fresh plant material. The techniques being used include FTIR, ^{13}C nmr and chemical methods. The results should aid utilization research in addition to structural studies.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

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| 354. THE PREPARATION AND CHARACTERIZATION OF
LIGAND TYPES INTERMEDIATE IN THE METAL-
CATALYZED CONVERSION OF COAL TO METHANE,
METHANOL, AND HIGHER ALKANES AND ALCOHOLS | \$80,000
16 mo. | 02-01 |
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- John A. Gladysz
Department of Chemistry

Homogeneous complexes containing ligand types believed to be intermediate in the metal-catalyzed conversion of carbon monoxide to organic molecules (methane, methanol, gasoline) are being prepared. Since carbon monoxide is readily available from coal, this research may provide insight as how to obtain petrochemicals from coal. Current work is focusing on the reactions and properties of rhenium formyl, hydroxycarbene, hydroxyalkyl, and carbene complexes. It has been shown that formyl complexes can undergo a facile disproportionation below room temperature when treated with electrophiles. Methyl ($-\text{CH}_3$) and carbonyl ($-\text{CO}$) complexes are produced. The stabilization of hydroxyalkyl complexes by chelation is being attempted. Numerous rhenium carbene complexes have been isolated, some of which can exist as two geometric isomers. Their reactions and photochemistry are under investigation.

Chemical Energy, continued

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

355. CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDIES OF HYDROCARBONS David M. Grant and Ronald J. Pugmire Departments of Chemistry and Fuels Engineering	\$83,000	02-01
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The two goals of this project are: 1) fundamental studies of hydroaromatic species in the liquid and solid states; and 2) examination of coal maceral concentrates. The former goal includes studies of T_1 processes and examination of dynamic processes and conformational properties elucidated from temperature dependent studies of model hydroaromatic compounds. This phase of the work has focused on liquid and solid chemical shift data on hydroaromatic derivatives of naphthalene, anthracene, and phenanthrene as well as their methyl derivatives. The second fundamental goal to study coal macerals has focused on the differences observed in chemical shift patterns between alginite, sporinite, vitrinite, and fusinite samples. Experiments will be carried out on maceral concentrates from a number of well characterized coals from differing coal provinces and differing ranks to assess the effects of rank paramaters and coal source on the chemical information obtained from NMR data.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

356. ORGANOMETALLIC CATALYSTS AND ANALOGS FOR CARBON-CARBON BOND CLEAVAGE REACTIONS IN HYDROCARBONS AND FOR CO REDUCTION Robert H. Grubbs Department of Chemistry	\$145,000 24 mo. FY80-81	02-01
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Catalysis of molecular hydrogen reduction of carbon monoxide to useful organic products via nucleophilic attack at transition metal bond carbon monoxide is being investigated. When $\text{Cr}(\text{CO})_6$ is treated with LiNMe_2 , a complex, $(\text{CO})_5\text{CrC}(\text{O}^-)(\text{NMe}_2)$, is produced which is hydrogenated in THF solution (35 psi H_2 , 130°C), to give low to moderate yields of methanol (~10%) and dimethylformamide (DMF, ~30%). If the same hydrogenation is carried out in hexamethylphosphoramide, a roughly stoichiometric amount of trimethylamine is obtained. Present evidence suggests intermediate formation of DMF and a chromium hydride anion which reduces DMF to trimethylamine. The postulated hydride, $[(\text{CO})_5\text{CrH}]^-$, has been prepared and shown to reduce a range of amides to the corresponding amines under the normal reaction conditions. Obvious extensions of this technology to related catalytic systems are being actively pursued.

Chemical Energy, continued

YALE UNIVERSITY
New Haven, Connecticut 06520

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| 357. | SELECTIVITY ACTIVITY AND METAL-SUPPORT
INTERACTIONS OF Rh BIMETALLIC CATALYSTS
Gary L. Haller
Department of Chemical Engineering | \$54,882 | 02-01 |
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The processing of coal into liquid and gaseous fuels is expected to put stringent demands on catalysts with regard to selectivity and activity maintenance. This program is designed to investigate the effects of a modifying second metal (Ag, Cu, Au, Ir and Pt) on the selectivity and activity of Rh supported catalysts. The latter two metals (Ir and Pt) form miscible-intergroup VIII catalysts with Rh in which all components are active. The other three metals (Ag, Cu and Au) are immiscible with Rh and are inactive for the test reactions used in this study (neopentane hydrogenolysis/isomerization and methanation). However, in both cases there are geometric and electronic effects on activity. The goal of this investigation is to understand the nature of the bimetallic interaction and to determine the dependence of the interaction on the oxide support. Catalysts are characterized by H₂/CO volumetric chemisorption (and programmed thermodesorption), X-ray photoelectron spectroscopy, infrared spectroscopy and extended X-ray absorption fine structure study of supported Rh bimetallic catalysts.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

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| 358. | METALLOCARBORANES STRUCTURALLY ENGINEERED
FOR THE REDUCTION OF CARBON MONOXIDE
M. Frederick Hawthorne
Department of Chemistry | \$110,000
24 mo.
FY80-81 | 02-01 |
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The purpose of this research project is to investigate the use of polymetallo-carboranes of several distinct structural types as catalysts for the homogeneous reduction of carbon monoxide with hydrogen. Like heterogeneous catalysts, such compounds have the potential for metal-metal cooperativity necessary for the reduction of carbon monoxide to hydrocarbons while retaining the advantages of mononuclear homogeneous catalysts. Representative members of each of three structural types of clusters containing boron, carbon, and two or more metal atom vertices are being synthesized and characterized. Emphasis is being given to metals such as rhodium and iridium with demonstrated activity in carbon monoxide reduction and to compounds containing early and late transition metals in the same molecule. Structural characterization by X-ray crystallography followed by screening for activity in catalytic processes involving carbon monoxide is being carried out on new complexes. Solution behavior is being studied by ¹H, ¹¹B and ³¹P NMR.

Chemical Energy, continued

RUTGERS UNIVERSITY
Newark, New Jersey 07102

359. STUDIES OF ELECTROLYTES IN LOW DIELECTRIC MEDIA \$31,500 02-01
Paul Hemmes
Department of Chemistry

Certain lithium salts, LiClO_4 and LiSCN , have been studied in solvents of low dielectric constant such as 0.50 mole fraction xylene-THF, dimethylcarbonate, diethylcarbonate, dipropylcarbonate and dibutylcarbonate. These salts were studied in dimethyl and diethylcarbonates using an electric field modulation technique, classical conductance and, in the case of LiSCN , infrared spectroscopy. The purpose of these measurements was to obtain information about ion pair dimerization (quadrupole formation). The ion pair formation constant, the triple ion formation constant and the quadrupole formation constant were all measured. The quadrupole formation constants were very small compared to the values which were obtained from dielectric measurements. This could be explained if the quadrupoles existed in a number of forms differing in the extent of solvation. It was found that the donor number of the solvent plays a large role in determining the extent of quadrupole formation. From the kinetic and conductance data it seems that dimethylcarbonate has a higher donor number than the other carbonates.

YALE UNIVERSITY
New Haven, Connecticut 06520

360. THE ROLE OF d-ELECTRONS IN CHEMISORPTION \$46,263 02-01
STUDIED BY ELECTRON SPECTROSCOPY
Victor E. Henrich
Department of Engineering and Applied Science

This research program is investigating the interaction of d-electron orbitals on various types of TiO_2 (rutile) surfaces with both chemisorbed molecules and with Group VIII metals supported on TiO_2 . Single-crystal TiO_2 surfaces are used so that chemisorption can be studied on surface sites whose electronic and geometric structure are well characterized. The surface cation d-orbitals, which are normally empty on perfect TiO_2 surfaces, can be partially populated by creating surface defects (Ti^{3+}/O -vacancy complexes). Charge transfer between the TiO_2 substrate and chemisorbed molecules or metal atoms and clusters (which are produced by evaporation of the catalyst metal onto the single-crystal samples in UHV) is determined by means of both x-ray and ultraviolet photoemission spectroscopy, and the surfaces are also characterized by Auger and electron-energy-loss spectroscopy and low-energy-electron diffraction. Changes in the electronic structure of supported metals upon chemisorption of simple molecules are also being investigated.

Chemical Energy, continued

UNIVERSITY OF PITTSBURGH
Pittsburgh, Pennsylvania 15260

361. STUDIES OF SUPPORTED METAL CATALYSTS	\$125,000	02-01
David M. Hercules	20 mo.	
Department of Chemistry	FY 81-82	

The purpose of this study is to understand how species on the surface of a heterogeneous catalyst are related to catalyst behavior. Surface spectroscopic techniques (ESCA, SIMS, ISS, Raman, EXAFS) are the major tools used; results are coupled with chemical studies. The effect of Zn^{+2} on Co/Al₂O₃ catalysts is to enhance formation of tetrahedral cobalt species, resulting in increased dispersion of Co. Studies of Co/Mo/Al₂O₃ catalysts show that Co does not disrupt the Mo monolayer but that a significant effect of Mo on Co is observed. No Co₃O₄ is observed up to 7% CoO but an "interaction" species between Co and Mo is observed. Research on W/Al₂O₃ catalysts has shown they are different from Mo/Al₂O₃ catalysts; no detectable Al₂(WO₄)₃ on the surface and the W-interaction species is not reduced by H₂. Bulk WO₃ is reduced to W-metal. Similarities between Mo/Al₂O₃ and W/Al₂O₃ are formation of tetrahedral and octahedral "interaction" species below monolayer coverage. Sequential formation of species is more clearly defined for W/Al₂O₃.

SRI INTERNATIONAL
Menlo Park, California 94025

362. HIGH TEMPERATURE CHEMISTRY OF HYDROGEN PRODUCTION CYCLES	\$41,356	02-01
D. L. Hildenbrand		
Materials Research Laboratory		

The objective of this program is to obtain fundamental thermodynamic and kinetic data for a variety of solid decomposition/vaporization processes pertinent to thermochemical hydrogen generation, as well as other energy technologies involving stack gas cleanup and hot corrosion. These decomposition processes are being studied by the torsion-effusion method and by high temperature mass spectrometry, so that both absolute pressure and vapor composition are determined. Primary emphasis is on the study of metal sulfate decomposition processes, most recently those of Mg, Cu, Na, and Fe, and particularly on the role of certain metal and oxide additives that are observed to catalyze many of the sulfate decompositions. These additives are believed to catalyze the SO₃-SO₂ equilibrium in the second stage of the decomposition process, and their effectiveness in catalyzing the direct decomposition of gaseous SO₃ also is being studied. The results yield accurate thermochemical and kinetic data needed for process design and for elucidation of basic mechanistic features.

Chemical Energy, continued

UNIVERSITY OF DELAWARE
Newark, Delaware 19711

363. AUGER AND REACTION STUDIES OF POISONING BY SULFUR AND REGENERATION OF METAL SYNTHESIS GAS CATALYSTS James R. Katzer Department of Chemical Engineering	\$200,000 24 mo. FY80-81	02-01
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This research program is developing a quantitative understanding of sulfur poisoning of synthesis gas conversion catalysts using a combination of surface characterization spectroscopies and reaction rate studies. Studies have shown that sulfur poisoning of Ni and Ru catalysts occurs purely by an active site blockage mechanism, whereas for Co and Fe sulfur poisoning involves both an electronic effect and site blockage. Fourier transform infrared and AES studies are being used to verify the role of electronic factors in carbon and sulfur poisoning of Ni and Co catalysts. Sulfur poisoning of highly dispersed supported Ni involves first adsorption of sulfur on the surface followed by incorporation into the subsurface layers. A patent on total regeneration of sulfur-poisoned catalysts resulting from the work has been issued.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

364. SOLID STATE, SURFACE AND CATALYTIC STUDIES OF OXIDES Harold H. Kung Department of Chemical Engineering	\$120,000 24 mo. FY80-81	02-01
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This research program aims at elucidating the dependence of the catalytic properties on the bulk and the surface state of oxides. Current emphasis is on transition metal oxides and zinc oxide. In the program involving zinc oxide, single crystal surfaces of the oxide on which regions of the surface behave like either anion or cation vacancies are being prepared by cutting surfaces which incline along the c-axis. Temperature programmed desorption/reaction is being used to monitor interaction of small molecules on these surfaces. In another program on mixed oxides of iron, the electronic effect of the second component on the properties of iron oxide in selective oxidative dehydrogenation of butene to butadiene is being investigated. Various second components are studied and their effect on the kinetics and the selectivity of the reaction is being monitored. The surface composition is also determined by Auger spectroscopy as a function of the bulk composition.

Chemical Energy, continued

TEXAS A&M UNIVERSITY
College Station, Texas 77843

365. A STUDY OF CATALYSTS AND MECHANISMS IN SYNTHESIS REACTIONS	\$130,000	02-01
Jack H. Lunsford	24 mo.	
Department of Chemistry	FY81-82	

Research on the role of metals in the catalytic synthesis of alcohols is currently being explored. Palladium, for example, is active for the formation of methanol from carbon monoxide and hydrogen; however, the selectivity of the reaction to methanol versus methane is strongly dependent on the nature of the support. With palladium on two different types of silica one may obtain almost pure methanol as the product or almost pure methane. Methanol is produced on the catalysts exhibiting small palladium crystallites on which CO is weakly adsorbed; whereas, the formation of methane is directly related to the density of acid sites at the surface of the support. In a separate study gas phase hydrocarbon radicals, formed at solid surfaces, are being trapped by matrix isolation techniques and identified by electron paramagnetic resonance spectroscopy. These radicals may be important intermediates in heterogeneous catalysis, as illustrated by the observation that gas phase π -allyl radicals formed over bismuth oxide constitute a primary pathway for the formation of 1,5-hexadiene.

STANFORD UNIVERSITY
Stanford, California 94305

366. MOLECULAR BEAM STUDIES OF THE DYNAMICS OF ACTIVATED ADSORPTION AND HETEROGENEOUS KINETICS ON SINGLE CRYSTAL SURFACES	\$145,000	02-01
Robert J. Madix	24 mo.	
Department of Chemical Engineering	FY81-82	

This research program is directed toward the understanding of reactive collisions between gas phase molecules and surfaces and between molecular species adsorbed on surfaces. Both steady state and modulated molecular beam techniques are being employed in combination with low energy electron diffraction and Auger spectroscopy to relate the nature of reactive scattering to surface structure and composition. The work is concentrated on reactions of simple molecules such as H₂, O₂ and CO. Of particular interest is the effect of sulfur adsorbed on stepped platinum surfaces on adsorption, surface reaction and desorption steps. An apparatus is being constructed for studying collisions of translationally hot molecules with surfaces.

Chemical Energy, continued

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

367. SUPPORTED f-ELEMENT ORGANOMETALLIC COM- \$54,000 02-01
PLEXES: SURFACE CHEMISTRY AND CATALYSIS
Tobin J. Marks and Robert L. Burwell, Jr.
Department of Chemistry

The goal of this project is to elucidate the surface chemistry and catalytic properties of highly reactive f-element (primarily actinide) organometallic compounds supported on metal oxides. The nature of the supported species is probed by a battery of chemical and physical techniques, to understand the nature of the adsorption process as well as how it varies with actinide identity (thorium or uranium), ligand identity, and support preparation. The catalytic properties of the supported organoactinides and how these can be tuned are also under investigation.

STANFORD UNIVERSITY
Stanford, California 94305

368. ELECTROCATALYTIC OXIDATION OF GASEOUS \$43,000 02-01
HYDROCARBONS ON SOLID-OXIDE ELECTROLYTES
David M. Mason
Department of Chemical Engineering

The goal of this research program is to obtain electrocatalytic data which will allow kinetics mechanisms to be established for selected hydrocarbons being oxidized on solid oxygen-ion type electrolyte anodes. A fundamental understanding of the kinetics of the electrode-electrolyte process is not only of scientific interest, but provides basic information useful in the design of such devices as fuel cells and oxygen sensors. Experimentation to date has shown the general reactivity of common fuel species: H₂, CH₃OH, CO, C₂H₅OH and CH₄ with the reactivity in descending order. The most important experimental result is that the electrolyte surface contains the active catalytic sites - not the porous electrode - be it Pt, Au, or non-noble metal. These sites are hypothesized to be colored-centers (trapped electrons) or holes and in continuing work emphasis is being placed on experiments such as employing radiation to test this hypothesis. Steady-state and transient measurements varying temperature reactant concentrations, and surface morphology are being obtained to elucidate the mechanisms.

Chemical Energy, continued

SRI INTERNATIONAL
Menlo Park, California 94025

369. ADSORPTION THERMODYNAMICS ON METAL CATALYST SURFACES	\$110,000 18 mo. FY81-82	02-01
Jon G. McCarty and Henry Wise Materials Research Laboratory		

The primary objective of this research program is to measure the heat and entropy of sulfur and chlorine chemisorption on metal surfaces in order to relate these thermodynamic parameters to the problem of catalyst poisoning. The binding energy, surface mobility and two dimensional structure are determined for sulfur and chlorine chemisorption on a variety of transition metal surfaces. A closed gas-recirculation system is used to measure sulfur adsorption equilibria on supported and unsupported metals and AES and LEED are used to determine the equilibrium sulfur and chlorine coverage on single-crystal surfaces following exposure to H₂S/H₂ and HCl/H₂ gas mixtures over a range of temperatures and surface coverage. Sulfur chemisorption isosteres have been measured for Fe, Co, and Cu and add to the previous results for Ni and Ru. The heats of formation of chemisorbed sulfur are considerably more exothermic at low coverage than the corresponding bulk sulfides but decline with increasing coverage and ultimately approach the bulk sulfide levels. Sulfur tolerance limits for metal catalysts are extremely low at temperatures typical of catalytic processing in methanation and Fischer-Tropsch synthesis.

SRI INTERNATIONAL
Menlo Park, California 94025

370. DETERMINATION OF FUNDAMENTAL THERMO- CHEMICAL AND KINETIC DATA FOR RADICAL SPECIES IMPORTANT IN COAL CONVERSION AND AROMATIC FUEL UTILIZATION	\$69,997	02-01
D. F. McMillen and D. M. Golden		

The fundamental goals of this project are (1) to measure the rates at which certain bonds in coal-related alkyl-aromatic structures undergo thermal cleavage under coal conversion conditions to form resonance stabilized radicals, and (2) to incorporate these rates and the resulting radical heats of formation into an empirical-theoretical framework for the estimation of heats of formation of benzylic and other coal-related radicals. The Very Low Pressure Pyrolysis technique has been used to measure the rate of unimolecular decomposition of 9-ethylanthracene and 9-ethylphenanthrene to give the corresponding arylmethyl radicals. The measured rates indicate that the resonance stabilization energies of these radicals are 19.2 and 13.9 kcal/mole, respectively, validating a recently proposed technique for rapid estimation of these values. The arylmethyl/methyl radical cross combination rates were determined to be ca. 4×10^9 l/mole-sec.

Chemical Energy, continued

UNIVERSITY OF SOUTHERN CALIFORNIA
Los Angeles, California 90007

371. SUPERACID CATALYZED DEPOLYMERIZATION AND CONVERSION OF COALS \$60,000 02-01
George A. Olah
Department of Chemistry

Superacids possess acidities up to a billion times stronger than conventional strong mineral acids, such as sulfuric acid. Novel, superacid catalyzed conversions of bituminous coals and lignites are being studied in order to increase the H/C ratio of coals. Reactions being studied include depolymerization reactions, alkylation and transalkylation reactions, acylation, nitration and reductive coupling reactions. Reactions with both liquid and solid superacidic catalyst systems are being investigated. Liquid superacidic systems are also being used for structural studies (using ^{13}C NMR spectroscopy) of the solubilized carbocationic components of coals. In order to obtain a better understanding of the basic chemistry of the superacid catalyzed conversion reactions, model systems, such as diphenylmethane, dinaphthylmethane and dianthracylmethane are also being studied under comparable reaction conditions.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

372. REACTIONS OF IRON ATOMS WITH MOLECULES IN LOW TEMPERATURE MATRICES \$52,658 02-01
Ralph G. Pearson and Paul Barrett
Departments of Chemistry and Physics

This project's goal is to study the reactivity of metal atoms and clusters in low temperature matrices containing reactive molecules. Mössbauer, infrared, and UV spectroscopies are used to identify the reaction products. Reactions between Fe, Fe₂, and iron clusters and low temperature matrix isolated molecules of N₂, CO, HI, CH₄, CH₂N₂ and other small molecules are under investigation. The reactions of other transition metals that are of importance to catalysis will also be studied.

Chemical Energy, continued

THE UNIVERSITY OF TEXAS
Austin, Texas 78712

373. DEVELOPMENT OF CATALYSTS FOR THE UTILIZATION OF CARBON MONOXIDE Rowland Pettit Department of Chemistry	\$125,000 24 mo. FY81-82	02-01
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It is generally agreed that the mechanism of the Fischer-Tropsch reaction is a polymerization process in which the chain growth involves a one-carbon atom addition to an alkyl fragment on a metal catalyst surface. Our results indicate that the nature of this one-carbon species is a methylene fragment (CH_2) and not a carbon monoxide molecule as proposed in the mechanism of Pichler and Schultz. Two independent lines of research support this view: (a) it is found that methylene fragments, when deposited on the Fischer-Tropsch catalyst surfaces, produce Fischer-Tropsch-type hydrocarbons when hydrogen is also present; and (2) when $^{13}\text{CH}_2$ groups are added to an ongoing Fischer-Tropsch reaction using ^{12}CO and H_2 the incorporation of ^{13}C into the hydrocarbons is consistent with chain growth involving CH_2 rather than CO . Experiments are now being directed at a determination of the initiation and termination steps of the Fischer-Tropsch polymerization process.

INDIANA-PURDUE UNIVERSITY/INDIANAPOLIS
Indianapolis, Indiana 46205

374. THE METAL-AMMONIA REDUCTION AND REDUCTIVE ALKYLATION OF COAL TAR HYDROCARBONS P. W. Rabideau Department of Chemistry	\$81,000 24 mo. FY80-81	02-01
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This research program involves an investigation of the mechanistic aspects of the reduction of aromatic compounds (especially coal tar hydrocarbons) by alkali metals in liquid ammonia. This reaction has important applications to coal chemistry since three chemical processes that occur under these conditions lead to a solubilization of coal: 1) hydrogenation of aromatic rings, 2) cleavage of carbon-carbon and carbon-oxygen bonds, and 3) introduction of alkyl groups by reductive alkylation techniques. Furthermore, the stereochemistry of both the carbanion intermediates as well as the reduced products is being studied by H-1 and C-13 NMR.

Chemical Energy, continued

MARQUETTE UNIVERSITY
Milwaukee, Wisconsin 53233

375. POLYMER-BASED CATALYSTS \$44,468 02-01
Steven L. Regen
Department of Chemistry

This research program is aimed at developing efficient, stable and selective polymer-based catalysts for accelerating aqueous phase--organic phase reactions. Current effort focuses on ionic and polyether-type resins; e.g. cross-linked polystyrene bearing pendant phosphonium, crown ether or polyether groups. Simple nucleophilic displacement reactions are being used to evaluate catalyst activity. Kinetic measurements are being performed by monitoring product mixtures using gas-liquid chromatography. Swelling measurements and ^{13}C NMR spectroscopy are being used to define the micro-environment within these resins. Of particular interest is understanding the relationship between macrostructure, microenvironment and catalyst activity.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

376. STUDIES ON UNUSUALLY REACTIVE METAL POWDERS. PREPARATION OF NEW ORGANO-METALLIC COMPOUNDS. \$60,140 02-01
Reuben D. Rieke
Department of Chemistry

This research program is involved with the preparation and study of highly reactive metal powders. The highly reactive metal powders are prepared by reduction of the corresponding metal salt. This approach works well for main group metals as well as transition metals. Highly reactive nickel, palladium, platinum, cobalt, and iron are currently under investigation. Highly reactive nickel powders rapidly react with aryl halides to either yield the coupled product or simple reductive cleavage. The course of the reaction is easily controlled by proper solvent choice. Highly reactive palladium and platinum rapidly react with pentafluoriodobenzene to yield an organopalladium or organoplatinum complex. These complexes yield a wide variety of new palladium or platinum complexes by reaction with numerous ligands.

Chemical Energy, continued

TEXAS A&M UNIVERSITY
College Station, Texas 77843

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| 377. THE INFLUENCE OF f-ELECTRON CONFIGURATION
ON CATALYTIC PROPERTIES OF LANTHANIDE
OXIDES | \$90,661
20 mo.
FY81-82 | 02-01 |
| Michael P. Rosynek
Department of Chemistry | | |

The intent of this research program is to identify and characterize correlations that exist between the physical/chemical properties of the lanthanide oxides and their corresponding catalytic behaviors. Current emphasis is being placed on investigations of the stoichiometric sesquioxides of lanthanum, praseodymium, and neodymium. The dual-pathway (dehydration/dehydrogenation) decompositions of alcohols are being used as diagnostic reactions to investigate the effect of periodic trends in certain solid-state parameters on the multi-site surface properties of these basic oxide catalysts. These studies are being supplemented by thermal analysis and adsorption measurements that are designed to characterize and optimize suitable catalyst preparation and pretreatment methods. Computer-assisted infrared spectroscopic studies of the interaction of selected probe molecules and reaction species with these oxides are furnishing information about the nature and behavior of various types of catalytic sites on their surfaces.

WASHINGTON STATE UNIVERSITY
Pullman, Washington 99164

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| 378. SYNTHETIC APPROACHES TO HOMOGENEOUSLY
CATALYZED OXIDATION REACTIONS | \$59,592 | 02-01 |
| D. Max Roundhill
Department of Chemistry | | |

This research effort is focused on the design of new homogeneous catalysts for application in oxidation reactions. Particular emphasis is being placed on the chemistry of transition metal carbonyls with oxygen, hydrogen peroxide, and organic peroxides. Both thermally and photochemically catalyzed oxidations of organic substrates are being researched, and intermediates are being probed by infrared and nuclear magnetic resonance techniques. The reactions of platinum metal oxo, hydroxo and hydroperoxo complexes are being investigated with particular emphasis being placed on non-radical oxygen atom transfer reactions. Hydrocarbon and sulfur substrates are being used in these reactions, and selectivity and catalytic efficiency of the process is being monitored by organic analytical techniques.

Chemical Energy, continued

RUTGERS UNIVERSITY
New Brunswick, New Jersey 08903

379. NATURE OF ODD-ELECTRON SPECIES AND THEIR ROLE IN SELECTED CATALYTIC PROCESSES \$52,486 02-01
Joseph San Filippo
Department of Chemistry

A series of radical anions, $[(\pi\text{-olefin})\text{Fe}(\text{CO})_3]^\cdot$, have been prepared and spectroscopically characterized (esr). With activated olefins, e.g. maleic anhydride, these species are obtained by reaction of the olefin with $\text{Na}_2\text{Fe}(\text{CO})_4$ or by reduction of the $(\pi\text{-olefin})\text{Fe}(\text{CO})_4$ complex with Na/K alloy or sodium naphthalide in THF. A closely related series of iron carbonyl radical anions is obtained by similar reductions of $(\text{diene})\text{Fe}(\text{CO})_3$ complexes at low temperatures in THF/HMPA solutions. Isotopic labelling studies employing ^{57}Fe and ^{13}C were also carried out.

UNIVERSITY OF KENTUCKY
Lexington, Kentucky 40506

380. FUNDAMENTAL STUDY OF CATALYSTS USING LASER RAMAN, INFRARED, AUGER ELECTRON SPECTROSCOPY AND LOW ENERGY ELECTRON DIFFRACTION \$140,000 02-01
23 mo.
FY 81-82
Gordon A. Sargent and E. B. Bradley
College of Engineering

The fundamental goal of this project is to develop an understanding of catalytic activity and selectivity with the long-range goal of producing better catalysts. The techniques of LEED, Auger spectroscopy, and laser Raman and infrared spectroscopies are being used to study the surface structure and bonding of CO , CH_4 , H_2 and O_2 adsorbed on $\text{Ni}(111)$ and $\text{Ni}(100)$ single crystal surfaces. The surface coverage is controlled by varying the gas pressure and exposure time. Surface dipoles (magnitude and orientation) are being measured for each gas adsorbed on the surface by a combination of work function change measurements and spectroscopic techniques. Laser Raman and infrared spectroscopy are used to determine vibrational modes of surface structures of the adsorbed molecules and the polarization of Raman bands and changes in band intensities are used to determine electric dipole orientation and thermal desorption characteristics.

Chemical Energy, continued

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

381. REDUCTION OF CARBON MONOXIDE	\$147,148	02-01
Richard R. Schrock	24 mo.	
Department of Chemistry	FY80-81	

This research program is designed to probe the question of how to reduce carbon monoxide with molecular hydrogen. The approach is to prepare hydride complexes of the earlier metals in high oxidation states and study how they will stoichiometrically reduce carbon monoxide. One type of molecule which is being looked at closely is one which contains more than one metal. New complexes are being characterized by conventional spectroscopic techniques. Reactions of new hydrido complexes with other small molecules (isonitriles, nitriles, olefins) are also being investigated. The ultimate goal is to discover a system which will catalytically reduce carbon monoxide with molecular hydrogen to give a two or more carbon product selectively.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

382. ORGANOMETALLIC CHEMISTRY OF WEAKLY SOL- VATED TRANSITION METAL CATIONS	\$50,000	02-01
Ayusman Sen		
Department of Chemistry		

An important requirement of homogeneous catalysts is that they have the ability to create vacant coordination sites by dissociation of weakly held ligands. Transition metal cations solvated in weakly coordinating solvents and having non-coordinating counter-anions should meet this criterion. Furthermore, the catalytic properties of such compounds should be subject to modification in a predictable way by the stepwise substitution of solvent molecules by other more strongly binding ligands. In this context, the catalytic chemistry of acetonitrile solvated transition metal cations are being examined, with the initial focus being on palladium, molybdenum and tungsten compounds. Preliminary indications are that the chemistry associated with these compounds differs very significantly from that observed for conventional, neutral transition metal compounds on one hand and traditional non-transition metal Lewis acids on the other. They appear to constitute a new class of catalysts for the polymerization of a wide range of olefinic and acetylenic compounds under unusually mild conditions. The mechanisms of these novel polymerization reactions are being investigated.

Chemical Energy, continued

COLORADO STATE UNIVERSITY
Fort Collins, Colorado 80523

383. PALLADIUM CATALYZED COUPLING REACTIONS: \$50,066 02-01
MECHANISM OF REDUCTIVE ELIMINATION
J. K. Stille
Department of Chemistry

Metal clusters can serve as models for metal surfaces in catalysis, and because the cluster is well defined and amenable to study by the methods and techniques available to homogeneous systems, the reactions on clusters can be studied in detail. Thus, a knowledge of the mechanisms of reactions that occur on clusters can provide a better understanding of heterogeneously catalyzed reactions and help in developing new heterogeneous catalysts. The synthesis of dinuclear platinum and palladium complexes containing alkyl groups on adjacent bonded metals, and the reactions of these complexes, particularly the 1,2-reductive elimination reactions are being carried out. Elucidation of the mechanism(s) of these reactions should provide a better understanding of how coupling, oligomerization and isomerization reactions of hydrocarbons take place on metal surfaces.

The Pennsylvania State University
University Park, Pennsylvania 16802

384. EFFECTS OF CRYSTALLITE SIZE AND THE \$132,255 02-01
SUPPORT ON ADSORPTIVE AND CATALYTIC
24 mo.
PROPERTIES OF METALS FY80-81
M. A. Vannice
Department of Chemical Engineering

This program is focused on the effects of metal crystallite size and metal-support interactions on the adsorption properties and catalytic behavior of Group VIII metals. An infrared cell has been designed to operate as a steady-state reactor thereby allowing IR spectra and kinetic data to be obtained simultaneously. In addition to this in situ characterization of adsorbed CO under reaction conditions, these Pt, Pd and Ni catalysts are also characterized by x-ray diffraction and chemisorption measurements. Specific activities have been found to vary by two orders of magnitude as a consequence of the type of support used to disperse the metal. In addition to the steady-state IR study of supported Ni catalysts, a new, small-volume IR cell is being built to allow transient studies of the different forms of adsorbed CO to examine their relative reactivity and desorbability. A new differential scanning calorimeter is being used to directly measure heats of adsorption of CO, H₂, and O₂ on these metals because results to date indicate that Strong Metal-Support Interactions (SMSI) exist which alter the adsorbed state of gases.

Chemical Energy, continued

THE PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

385. GASIFICATION OF DISORDERED CARBONS (CHARS)	\$140,000	02-01
Philip L. Walker, Jr. and R. G. Jenkins	24 mo.	
Department of Materials Science and Engineering	FY81-82	

Rate constants for the adsorption and desorption steps in the over-all gasification of carbons in oxygen are being measured as a function of carbon burn-off, both in the absence and presence of a catalyst (platinum). Kinetics for the adsorption step are being followed at low pressures, where gasification rates are proportional to oxygen pressure and unoccupied active surface area. Kinetics for the desorption step are being followed at elevated pressures where gasification rates are independent of oxygen pressure and directly proportional to the total concentration of active sites. Companion studies are being conducted in the presence of a 1% loading of platinum. Rate constants are being determined per unit of platinum surface area, using small angle x-ray scattering, and electron microscopy to characterize metal dispersion. The activity of active carbon sites in the absence of gasification is also being measured during the exchange reaction between CO_2^{16-16} and CO_2^{18-18} to produce CO_2^{16-18} .

YALE UNIVERSITY
New Haven, Connecticut 06511

386. ENERGIES OF ORGANIC COMPOUNDS	\$70,000	02-01
Kenneth B. Wiberg		
Department of Chemistry		

This project is concerned with the factors which control the energies of organic compounds. A major, and poorly understood, factor is the steric interaction between heteroatoms and alkyl groups and chains. As part of a study of these interactions, the hydration of alkenes is being studied. This gives both much improved enthalpy differences among alkenes, and the differences in energy among groups of alcohols. Reactions are being developed which should permit the determination of enthalpies of reduction of ketones and enthalpies of reduction of alkenes using homogeneous catalysts. In each case, a major goal is to obtain very precise data so that the interactions among groups may be studied in detail. Other systems being studied include the acetolysis of cyclopropanes and the hydrolysis of orthoesters. In addition, the Coulombic interactions are being studied via ab initio calculations, and molecular mechanics calculations are also being carried out.

Chemical Energy, continued

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

387. STUDY OF HETEROGENEOUS CATALYTIC CHEMISTRY \$150,000 02-01
ON TRANSITION METALS
John T. Yates, Jr.
Surface Science Division

This program consists of a multiprobe study of the molecular nature of heterogeneous catalytic chemistry. It involves four areas of research which have a common theme -- the investigation of surface processes on transition metal surfaces which are related to technologically important catalytic chemistry. These areas are 1.) Kinetics and mechanisms of catalytic reactions involving H₂ and CO. These studies are conducted with an apparatus which combines a high pressure reaction chamber with a surface analysis (predominantly AES) chamber. 2.) Neutron inelastic scattering spectroscopy (NIS) of catalysts. These investigations of the vibrations of surface species is progressing toward the use of NIS as an in situ probe of a catalyst surface under reaction conditions. 3.) The chemistry of water at surfaces--of fundamental importance in a number of areas-- is being studied with a combination of two ultra high vacuum techniques (ESDIAD and EELS). 4.) The adsorption and decomposition of small organic molecules on single crystal surfaces is being studied with a variety of UHV techniques with the long range objective of supplying a systematic picture of functional group stabilities on metal surfaces.

Separations

UNIVERSITY OF MINNESOTA
 Minneapolis, Minnesota 55455

388. CONTINUOUS CHEMICAL REACTION CHROMATO-
 GRAPHY \$44,761 02-02
 Rutherford Aris and Robert W. Carr, Jr.
 Department of Chemical Engineering and
 Materials Science

An experimental investigation of the catalytic dehydrogenation of cyclohexane over Pt/Al₂O₃ (60-80 mesh) in a rotating cylindrical annulus continuous chromatographic reactor was completed. A mathematical model of the reactor was developed and used for numerical simulation of reactor performance. Reaction yields in excess of equilibrium at the inlet conditions were obtained due to chromatographic separation of the products in the reactor. An investigation of the catalytic dehydration of tert-butyl alcohol over alumina was completed. The kinetics of the reaction were found to be zero order. Arrhenius parameters were determined. A preliminary study of a countercurrent moving bed continuous chromatographic reactor was done. An experimental apparatus for conducting countercurrent moving bed continuous chromatographic reactions is under construction. Also, some aspects of the mathematical theory of countercurrent chromatography have been considered.

BEND RESEARCH, INC.
 Bend, Oregon 97701

389. FUNDAMENTALS OF COUPLED-TRANSPORT
 MEMBRANES \$69,953 02-02
 W. C. Babcock

This program is aimed at determining the important parameters controlling coupled transport of uranium through liquid membranes. The membranes consist of a microporous polymeric support with a liquid complexing agent held within the pores by capillary forces. When this liquid membrane is interposed between two aqueous solutions of unequal ion concentrations, the complexing agent can pick up the ions on one side of the membrane and carry them across the membrane by diffusion in the form of a neutral complex. Ions of opposite charge may be carried in the same direction, or ions of like charge may be carried in the opposite direction. The coupling of the flows of two ions permits one of the ions to be pumped from a dilute to a concentrated solution. Furthermore, the membranes are selective, due to the selectivity of the complexing agent toward uranium over other metals. Thus, coupled transport is of potentially practical value in hydrometallurgy and in the treatment of radioactive wastes.

Separations, continued

STATE UNIVERSITY OF NEW YORK/STONY BROOK
Stony Brook, New York 11794

392. FUNDAMENTAL STUDIES IN ISOTOPE CHEMISTRY Jacob Bigeleisen Department of Chemistry	\$108,489	02-02
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Experimental and theoretical investigations are being made of isotope effects in chemical and physical processes. Theoretical studies probe the relationship between isotope effects and molecular structure and molecular forces. The contributions of stretching and bending motions in a variety of molecules, e.g. alkanes, alkenes, aromatics, CO₂, H₂O, to the isotopic reduced partition ratio for light and heavy atom isotopic substitution are being studied by the WIMPER(2) expansion. Systematic relations in the isotope chemistry of hydrogen with all elements of the periodic table are under investigation by the analysis of the differences in the free energies of formation of protium and deuterium compounds. Correlations are being made with molecular structure and the position in the periodic table of the elements combined with hydrogen. Direct measurements of the liquid-vapor isotope fractionation factors in methane and fluoromethanes are underway to elucidate the perturbations of molecular vibrations in the condensed phase by intermolecular forces.

BRIGHAM YOUNG UNIVERSITY
Provo, Utah 84602

393. SEPARATION OF ALKALI, ALKALINE EARTH AND RARE EARTH CATIONS BY LIQUID MEMBRANES CONTAINING MACROCYCLIC CARRIERS James J. Christensen Thermochemical Institute	\$72,500 15 mo. FY81-82	02-02
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This research program studies the use of macrocyclic ligands such as crown ethers and cryptands as carriers of cations through hydrophobic liquid membranes. These ligands are noted for their high degree of selectivity among alkali and alkaline earth cations, and this selectivity may be exploited in liquid membrane systems to effect cation separations. Stirred, bulk chloroform membranes are being used to screen the macrocycles for cation selectivity. These membranes also provide a well defined system to study the characteristics of cation transport of this type. A mathematical model has been developed to describe this membrane transport and is being tested against experimental transport data. In other experiments, macrocyclic carriers are also incorporated into supported 'diaphragm' membranes in which the liquid membrane is suspended on a thin porous polymer diaphragm, and into liquid surfactant or 'emulsion' membrane systems. The latter two membrane configurations offer high surface areas and short diffusion paths necessary to allow large cation fluxes for efficient separations.

Separations, continued

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

394. MULTIHETEROMACROCYCLES THAT COMPLEX METAL IONS \$108,840 02-02
Donald J. Cram
Department of Chemistry

This research involves the design, synthesis, and evaluation of cyclic organic compounds that selectively complex metal salts and solubilize them in organic solvents. Spherands are the only known synthetic ligand systems that, in the complexed state, contain cavities lined with electron pairs. They are composed of rigid carbocyclic frameworks that place heteroatoms in spherical arrangements around enforced cavities. Spherands are being studied that are composed of six or eight anisyl units attached to one another in a ring through aryl-aryl bonding in their 2,6-positions. They are highly cation selective in forming metallospherium salt complexes of unusual stability. Hemispherands are hybrids of spherands and crown ethers. Many spherands and hemispherands are being prepared and examined which contain anisyl, methoxycyclohexyl, urea, pyridine, pyridine oxide, and amide units. Metal ion and isotope-specific complexing agents are sought.

NAVAL RESEARCH LABORATORY
Washington, DC 20375

395. XENON/KRYPTON ELEMENTAL PHOTOCHEMICAL SEPARATION \$65,000 02-02
Terence Donohue
Laser Physics Branch

Mixtures of the noble gases xenon and krypton are separated by selective photochemical formation of their fluorides. Conditions are set so that only xenon will undergo reactions with the photochemically produced fluorine atoms and will thus precipitate from the gas mixtures as crystalline XeF_2 . Photochemical sources employed include a medium-pressure mercury lamp (366 nm) and a XeF excimer laser (351 nm). Separation factors (the purity of the product XeF_2) have been measured to be as high as 6000 and yields of enriched Xe can exceed 99.0%. Xenon and krypton constitute most of the offgases from nuclear reactors and reprocessing plants. These results indicate that this method could be employed for the removal of radioactive ^{85}Kr from stable xenon with purity sufficient (in a single-pass separation) to allow use and sale of the xenon. This work is now being extended from batch separations in static systems to continuous separations in a flowing systems which are more amenable to large-scale operation.

Separations, continued

UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

396. CHELATING EXTRACTANTS OF IMPROVED SELECTIVITY \$66,192 02-02
Henry Freiser
Department of Chemistry

This research program is dedicated to the development of chelating extractants of improved selectivity, particularly those capable of completely separating individual lanthanides. On the basis of a preliminary pattern recognition study of lanthanide chelate stability, several promising chelating extractants were selected and their equilibrium extraction behavior is now under study. In particular, the extraction behavior of 8-quinolinol and several of its derivatives with a series of representative trivalent lanthanide ions is being investigated. A systematic evaluation of the role of substituents in both the stability and selectivity is under way. The results of this investigation will be used to further refine the insights obtained through the pattern recognition study in the relationship between the molecular structure of the extractant and improvements in selectivity. The results obtained will also be relevant for developing improved separations of actinides.

HARVARD UNIVERSITY
Cambridge, Massachusetts 02138

397. ELECTRONIC STRUCTURE OF HELIUM AND HYDRIDE COMPLEXES \$47,000 02-02
Dudley R. Herschbach
Department of Chemistry

Theoretical calculations are nearly complete for the electronic structure of weakly bound complexes of the form $X(H_2)_n$ with $X=HeH^+$, H_2 , and H^- and $n = 2, 3, 4$. The results indicate that such complexes have sufficient binding energy to account for enhanced solubility of 3He in liquid tritium observed in experiments at Los Alamos. However, it remains puzzling how such weak complexes could persist without displacement of He by solvent molecules. To estimate the effect of the liquid environment, calculations are being pursued employing a "bubble" or "box" model like that previously applied to the solvated electron as a means to examine the role of the internal pressure of the liquid. Molecular beam experiments are in progress to produce a $(H^-)(H_2)_n$ complex by a collisional charge-transfer method.

Separations, continued

STATE UNIVERSITY OF NEW YORK/STONY BROOK
Stony Brook, New York 11794

398. STABLE ISOTOPE STUDIES \$109,450 02-02
Takanobu Ishida
Department of Chemistry

This research program consists of basic and developmental studies of various methods for the fractionation of stable isotopes and theoretical investigations of multiphase isotope effects to provide the proper foundation for the isotope separation studies. Fractionation of nitrogen isotopes by an exchange between gaseous nitric oxide and liquid dinitrogen trioxide is being studied in a stainless steel, counter-current, packed column to demonstrate and understand possibly higher separation factors and lower heights of effective theoretical plates with increasing column pressure. Product refluxers for the Nitrox process for nitrogen-15 separation that would not require chemical feeds and wastes are being investigated. To elucidate fundamental relationships between separation factors in distillation processes and the constitution of the working fluid, effects of temperature on the relative vapor pressures of pure, isotopically labelled fluoromethanes (^{13}C -, ^{12}C -, D-, and H- substitutions in methyl fluoride and methylene difluoride) are being studied using differential manometry in a precision cryostat.

UNIVERSITY OF GEORGIA
Athens, Georgia 30602

399. A STUDY OF MECHANISMS OF HYDROGEN \$66,933 02-02
DIFFUSION IN SEPARATION DEVICES
M. Howard Lee
Department of Physics

The diffusion of hydrogen isotopes in transition metals is highly selective and does not follow the classical pattern at low temperatures. The hydrogen diffusion property if properly understood can be a basis for isotope separation devices applicable to nuclear fusion reactors, hydrogen purification, heavy-water enrichment. To explore these possible applications, a study of the hydrogen transport mechanisms in Pd has been carried out by constructing a quantum statistical model of the lattice hydrogen. The hydrogen-metal system shows well defined phase transitions and mean-field-like critical behavior. The model for the cooperative hydrogen diffusion shows that it is isomorphic to models of magnetism for biquadratic exchange spin interaction. Thus the phases of H/Pd can be described by dipolar and quadrupolar ordering and the phase transitions in H/Pd in terms of the order parameters for the magnetic models. Our analysis suggests that the miscibility gap holds a key to understanding the A phase of H/Pd, where most of practical transport processes take place.

Separations, continued

KENT STATE UNIVERSITY
Kent, Ohio 44242

400. ADSORPTION AND DESORPTION OF HYDRO-
CARBONS AT LOW CONCENTRATIONS \$53,700 02-02
Richard Madey
Department of Physics

The objectives of this research are to investigate the physiochemical properties of isothermal adsorption of hydrocarbon gases and gas mixtures on absorbents and to study the dynamics of adsorption and desorption of adsorbates in adsorber beds. More specifically, these studies include: (1) Measurements of the transmission (or normalized outlet concentration) of a single adsorbate or mixtures at various concentrations, temperatures, and flow rates through selected adsorbates. (2) Analysis of the data on the time-dependent transmission in terms of appropriate mass-transfer models, and a study of the effects of interference on mass-transfer mechanisms. (3) A study of the physiochemical properties of adsorption in order to obtain correlations between molecular properties and important design parameters such as adsorption isotherms and longitudinal diffusion coefficients. (4) Computer simulation of experimental results to compare the experimental profiles with the calculated profiles.

TEXAS SOUTHERN UNIVERSITY
Houston, Texas 77004

401. SOLVENT EXTRACTION STUDIES USING HIGH-
MOLECULAR-WEIGHT AMINES \$45,581 02-02
Curtis W. McDonald
Department of Chemistry

The objective of this research is to develop efficient, simple and economic methods to remove trace quantities of metal ions, especially toxic metal ions such as mercury, lead, cadmium and nickel from aqueous solutions via high-molecular-weight amine liquid-liquid extraction and/or surfactant-foam separation. Of utmost concern is developing methods which require a minimum of energy and are amenable to scale-up for removal of metal ions from industrial wastewater. The associated chemistry is also being investigated. High-molecular-weight tertiary amines proved to be excellent reagents for liquid-liquid extraction whereas certain high-molecular-weight quaternary ammonium salts are excellent reagents for surfactant foam separation techniques.

Separations, continued

UNIVERSITY OF MINNESOTA
St. Paul, Minnesota 55108

402. INTERFACIAL CHEMISTRY IN SOLVENT
EXTRACTION SYSTEMS \$75,000 02-02
Ronald D. Neuman
Department of Forest Products

The goal of this research program is to further our fundamental understanding of the complex chemistry involved in the solvent extraction of metal ions from an aqueous phase to a nonpolar organic phase. Our approach to examining the solvent extraction process is monomolecular film studies of the behavior of extractant molecules and their interactions with metal ions using recently developed techniques employing lasers. A state-of-the-art laser heterodyne light-scattering apparatus is being further developed to investigate the desorption behavior of extraction reagents at liquid/vapor and liquid/liquid interfaces in order to provide valuable information on the structure and dynamics of extractant molecules in interfacial systems. Reliable desorption kinetics are to be obtained initially for two types of long-chain organic acids, carboxylic acids and alkyl phosphoric acids, with and without various metal ions in the aqueous phase. The development of an *in situ* technique for determining the interfacial chemical composition also is being attempted employing laser Raman spectroscopic techniques.

UNIVERSITY OF GEORGIA
Athens, Georgia 30602

403. FUNDAMENTAL STUDIES OF SEPARATION
PROCESSES \$72,000 02-02
L. B. Rogers
Department of Chemistry

This work is directed toward two different goals. First, basic studies are being directed toward the optimization of recycle gas chromatography, a technique that is useful on a small preparative scale for separating pairs of very similar compounds. Another basic study is aimed toward exploring a computerized method for estimating the amount of information conveyed by a complex chromatogram, regardless of whether gas or liquid chromatography is employed. The second major goal is directed toward problems involving complex mixtures of difficult-to-separate species. In one case, vanadium-containing chelates in Venezuelan crude oil are being fractionated using liquid chromatography prior to identification. Another difficult type of separation under investigation involves mixtures of oligomers which are found in samples of commercial polystyrene. Both types of mixtures involve subtle differences in solvent-solute and solute-adsorbent interactions.

Separations, continued

SYRACUSE UNIVERSITY
Syracuse, New York 13210

404. MECHANISMS OF GAS PERMEATION THROUGH POLYMER MEMBRANES S. Alexander Stern Department of Chemical Engineering and Materials Science	\$75,836 15 mo. FY81-82	02-02
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The objective of this study is to assess the validity of a "free-volume" model of gas permeation through nonporous polymer membranes. Permeability coefficients for CH_4 , CO_2 , C_2H_4 , and C_3H_8 in polyethylene estimated from the model were in satisfactory agreement with experimental values determined between 5° and 35°C., and at pressures of up to 40 atm. A new method of estimating permeability coefficients for gas mixtures from the free-volume model has been developed. Theoretical permeability coefficients for C_2H_4 - C_3H_8 , CO_2 - C_2H_4 , and CO_2 - C_3H_8 mixtures in polyethylene agreed satisfactorily with experiments. Simple correlations have been found for 3 characteristic free-volume parameters as a function of basic physicochemical properties of penetrant-polymer systems. These correlations are useful for predictive purposes. The free-volume model has now been extended to describe gas permeation through polymers both above and below their glass transition temperature.

ILLINOIS INSTITUTE OF TECHNOLOGY
Chicago, Illinois 60616

405. SELECTIVE METAL ION EXTRACTION FOR MULTIPLE ION LIQUID-LIQUID EXCHANGE REACTIONS Lawrence L. Tavlarides Chemical Engineering Department	\$53,995	02-02
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This research in hydrometallurgical solvent extraction is to develop a fundamental means to predict selectivity during simultaneous solvent extraction of multiple metal ions when kinetic rates and thermodynamic equilibria do not favor the desired metal. The chemical kinetics and thermodynamic chemical equilibria models for the system copper-iron-acid sulfate solutions extracted by β -alkenyl-8-hydroxy quinoline in xylene are being determined. A thermodynamic model for the chemical equilibria of copper is obtained from a regression analysis of data. The model considers the aqueous phase ionic equilibria and accounts for impurities in the extractant. Kinetic studies are conducted on the novel liquid jet recycle reactor for the copper system. The selected rate model is supported by a mechanism which assumes an interfacial reaction in which the rate limiting step is the formation of CuR^+ . Equilibria and kinetic studies for the iron system are in progress.

Separations, continued

SYRACUSE UNIVERSITY
Syracuse, New York 13210

406. PARTICLE DEPOSITION IN GRANULAR MEDIA	\$88,020	02-02
Chi Tien		
Department of Chemical Engineering and Materials Science		

This study is intended to obtain a fundamental and quantitative understanding of the particle deposition process arising from the flow of aerosol suspensions through granular media. Emphasis is placed on the transient behavior of the deposition process and the effect of deposited particles on deposition and flow. Both theoretical and experimental investigations are involved. The theoretical analysis is centered in the formulation and development of a simulation model capable of predicting the dynamic behavior of particle deposition in its entirety. The experimental work covers two topics: (A) The determination of the collection efficiency and pressure drop necessary to maintain a constant flow rate corresponding to various degrees of deposition and (B) the in-situ observation of particle deposition with the use of a two dimensional model filter.

UNIVERSITY OF HOUSTON
Houston, Texas 77004

407. MECHANISMS OF CAKE FILTRATION	\$144,999	02-02
Frank M. Tiller		
Chemical Engineering Department		

This project is aimed at developing the theory of particulate separation involving compressible, porous beds or sediments as found in filtration, centrifugation, and sedimentation. A key feature of the investigation involves close collaboration between the University of Houston and Martin-Marietta Laboratories. Generation of reliable data under well-defined conditions and integrating the areas of pretreatment, thickening, and separation are objectives of the research. Particle characteristics are being related to suspension behavior and cake structure. Sedimentation rates and cake structure are being correlated. The initial structure of deposits as affected by surface charge, suspension concentration, and agitation is being studied in relation to resistance to flow. Included in the program are internal flow mechanisms involving porosity and pressure distribution. Fine particle migration is being related to cake and medium blinding. Rheological and electrophoretic properties of suspensions are being correlated with separation behavior.

Separations, continued

COLUMBIA UNIVERSITY
New York, New York 10027

408. UTILIZATION OF MAGNETIC EFFECTS AS A MEANS OF ISOTOPE ENRICHMENT \$66,000 02-02
 Nicholas J. Turro
 Department of Chemistry

This research program is directed toward the development of 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 which allow the separation of isotopes which possess a finite magnetic moment from those which 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 photolysis of dibenzylketone in micellar solution has been demonstrated to be an efficient method for the separation of ^{13}C from ^{12}C and this system has the potential to serve as a practical method for obtaining samples of compounds that are strongly enriched in ^{13}C . The thermolysis of endoperoxides has been demonstrated to be a novel method of the selective separation of ^{17}O from ^{16}O and dependent on the application of a laboratory magnetic field.

UNIVERSITY OF CALIFORNIA/IRVINE
Irvine, California 92717

409. STUDIES OF ISOTOPIIC MASS EFFECTS IN CHEMISTRY \$72,074 02-02
 Max Wolfsberg
 Department of Chemistry

This project deals with theoretical studies of isotopic mass effects on the physical and chemical properties of molecules. Most such theoretical work is carried out within the Born-Oppenheimer approximation. Corrections to this approximation are now being explored; to this end, complete quantum mechanical Hamiltonian operators in useful forms are being constructed for polyatomic molecules. Application of statistical mechanics to the evaluation of equilibrium constants of isotopic exchange reactions requires the rotational-vibrational energy levels of molecules and isotope effects thereon. Theoretical calculations of these energy levels for ammonia and water are being carried out by variational methods and by perturbation methods. An understanding of infrared spectra of liquids is needed in order to understand isotope effects on vapor pressures; the effect of the surrounding medium on the absorption of electromagnetic radiation by a molecule is being studied. Statistical mechanical perturbation theory is being employed to gain an understanding of isotope effects.

Separations, continued

THE AEROSPACE CORPORATION
Los Angeles, California 90009

410. ISOTOPICALLY SELECTIVE, TWO-STEP PHOTODISSOCIATION
P. F. Zittel
Chemistry and Physics Laboratory
- \$93,394
- 02-02

The object of this program is an understanding of the photophysics, energy transfer processes, and chemistry of isotopically selective, two-step laser photodissociation of polyatomic molecules. Emphasis is placed on the separation of "middle" isotopes (e.g., ^{17}O and ^{33}S) which are difficult to separate cleanly using current techniques. Isotopically selective vibrational excitation of a small polyatomic molecule such as carbonyl sulfide (OCS) with an infrared laser, followed by photodissociation with an ultraviolet laser and chemical scavenging of the photo fragments, produces products enriched in the chosen atomic isotope. Isotope enrichments and product yields are studied as a function of various experimental parameters. Analysis by an extensive computer model interprets the results in terms of fundamental molecular processes and predicts optimum experimental conditions. Various isotopes of C, O, S and Br have been enriched using this technique. The critical photodissociation cross sections of several vibrationally excited molecules have been measured, as well as rate constants for various isotope-scrambling reactions.

Analysis

UNIVERSITY OF MASSACHUSETTS
Amherst, Massachusetts 01003

411. DYNAMICS OF, AND HEAT AND MASS TRANSFER IN, AN INDUCTION PLASMA Ramon M. Barnes Department of Chemistry	\$70,000 15 mo. FY81-82	02-03
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This project involves the computer modeling of the flow, temperature, concentration, and spectral radiation fields in an inductively coupled plasma discharge operated at atmospheric pressure in argon and in the presence of nitrogen under conditions popular in commercial configurations employed as a spectral excitation source. Particular emphasis is placed on the computation of the trajectories and temperature histories of solid particles or liquid droplets injected into the discharge. A new algorithm based upon solving transient rather than steady state continuity, momentum, and energy equations in terms of velocity and temperature rather than stream function, vorticity, and enthalpy will be extended to turbulent flow conditions which may exist with high aerosol carrier flow rates. Moreover, treatment of non-local thermodynamic equilibrium conditions is included.

BROWN UNIVERSITY
Providence, Rhode Island 02912

412. PHOTOCHEMICAL GENERATION OF THE OPTO- ACOUSTIC EFFECT Gerald J. Diebold Department of Chemistry	\$83,328	02-03
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This research is directed toward investigating the optoacoustic effect as a tool in studies of chemical kinetics. Mathematical analyses of several straightforward chemical reaction schemes have been carried out and predictions made regarding the behavior of the optoacoustic phase lag and signal amplitude. Photochemical systems are being investigated using a modulated, continuous visible dye laser and non-resonant spectrophone cell to verify these predictions. The most dramatic effects, that is, those peculiar to second order recombination kinetics, should be found in the behavior of the acoustic phase lag. Research is also being initiated on "chemical amplification" of optoacoustic signals. Here, chain reactions release large amounts of stored chemical energy into the acoustic wave. Detailed calculations have shown that the optoacoustic method should provide a direct measure of the photochemical chain length. The optoacoustic effect possesses a unique response to total reaction exothermicity and extremely high sensitivity that it should be used to advantage in studies of chemical kinetics.

Analysis, continued

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

413. FOURIER TRANSFORM PHOTOACOUSTIC SPECTROSCOPY Edward M. Eyring Department of Chemistry	\$58,882	02-03
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Fourier transform infrared photoacoustic spectroscopy (FTIRPAS) is a new method of measuring absorption of electromagnetic radiation by solid surfaces. This research seeks to resolve practical problems such as source intensity normalization, avoidance of signal saturation, sample cell construction, interfering absorption by gas phase species, and microphonic or piezoelectric detector selection that have limited the impact of FTPAS on the elucidation of heterogeneous catalysis. Spectra being obtained photoacoustically of organic molecules adsorbed on silica-alumina surfaces show FTIRPAS to be more useful than IR transmission spectroscopy for distinguishing between Lewis and Bronsted acid sites on catalytic surfaces. The initial/boundary value problem describing a megahertz frequency pulsed PA experiment is being solved via a new multi-level adaptive technique (MLAT). Numerical results are being compared with high frequency pulsed laser PA experiments to circumvent saturation effects at low chopping frequencies. Ultraviolet synchrotron PA experiments are also being explored.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

414. REACTIONS OF METAL IONS AND THEIR CLUSTERS IN THE GAS PHASE USING LASER IONIZATION- ION CYCLOTRON RESONANCE SPECTROSCOPY Ben S. Freiser Department of Chemistry	\$65,000	02-03
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The development of a combined pulsed laser source-ion cyclotron resonance spectrometer has proven to be a convenient and powerful method for generating and studying metal ions in the gas phase. Based on this technique the following areas are being investigated: (I) coordination and chelation, comparison of gas phase to solution; (II) metal ions as chemical ionization reagents; (III) metallic cluster ions and catalysis, structure and reactivity; and (IV) implications to proposed mechanisms of cationization in SIMS and related techniques. A state-of-the-art NICOLET FTMS prototype spectrometer recently put into operation will be employed in these studies.

Analysis, continued

THE AEROSPACE CORPORATION
El Segundo, California 90245

415. GAS PHASE ENERGY TRANSFER STUDIES BY LASER- \$49,966 02-03
EXCITED NONRESONANT FLUORESCENCE SPECTROSCOPY 10.5 mo.
J. A. Gelbwachs
Chemistry and Physics Laboratory

Laser-induced nonresonance fluorescence spectroscopy has recently provided single-atom detection limits and volumetric detection ratios of 1 part in 10^{17} . The method also provides a powerful means for the study of energy transfer processes that involve excited state atoms and various collision partners. The proposed work seeks to utilize the method for fundamental studies of the energy transfer processes that control atomic fluorescence detection limits. A systematic study of the differences in excited-state population redistribution in trivalent atoms that undergo collisions with rare gases and diatomics will be undertaken. Besides the obvious value of these studies to improved trace analytical detection, the electronic to vibrational transfer rates, collisional cross sections, and spin selection studies will provide data to assist in the understanding of the range and the nature of interaction potentials between excited state atoms and both rare gases and diatomics.

UNIVERSITY OF MARYLAND
College Park, Maryland 20742

416. NON-DESTRUCTIVE DETERMINATION OF \$95,000 02-03
TRACE-ELEMENT CONCENTRATIONS
Glen E. Gordon, William B. Walters,
and William H. Zoller
Department of Chemistry

This research program is designed to develop an instrumental nuclear method of analysis, neutron-capture prompt γ -ray activation analysis (PGAA). Earlier in the project, a neutron-beam facility was constructed at the National Bureau of Standards reactor. Samples are placed in the beam and prompt γ rays emitted following neutron captures by nuclei in the sample are observed between 0.1 and 11 MeV with a Ge(Li) detector surrounded by a NaI Compton-suppression crystal. Concentrations of most or all of the following elements can be measured in coal, fly ash, rocks and volcanic debris: H, B, C, N, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Cd, Sm and Gd. PGAA is an excellent tool for geochemical studies, as concentrations of all major species normally measured in rocks except phosphorus can be measured instrumentally during 2-hr irradiations. The focus of the present year's work is on application of PGAA to biological samples and the development of off-line applications based on the use of ^{252}Cf neutron sources.

Analysis, continued

UNIVERSITY OF VIRGINIA
Charlottesville, Virginia 22901

417. THE GLOW DISCHARGE AS AN ATOMIZATION AND IONIZATION SOURCE W. W. Harrison Department of Chemistry	\$59,395	02-03
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The primary thrust of this research is the study of the glow discharge plasma as an atomization/ionization source in analytical mass spectrometry. The fundamental sputtering mechanisms and the subsequent ionization of these sputtered neutral atoms in the plasma are of interest relative to their role in analytical chemistry, specifically trace element analysis. Different plasma ion source designs are being studied with particular interest in the ion beam stability, sputtered-atom to discharge-gas ratio, and net elemental sensitivity attainable. NBS alloy standard reference materials are being used to evaluate the overall analytical methodology.

THE UNIVERSITY OF WYOMING
Laramie, Wyoming 82071

418. SOLID SURFACE LUMINESCENCE ANALYSIS Robert J. Hurtubise Chemistry Department	\$62,977	02-03
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The main goals of this project are to discover the experimental conditions and to clarify the solid surface interactions needed for strong luminescence signals from organic compounds adsorbed on surfaces so as to advance the approach in organic trace analysis. Several phenolic type compounds are being adsorbed on polyacrylic acid-NaBr mixtures, filter paper and silica gel to induce room-temperature phosphorescence and fluorescence signals. The nature of the interactions responsible for the luminescence signals are being investigated with reflectance, infrared, and luminescence spectroscopy. Luminescence polarization and phosphorescent lifetime experiments are also being performed. Similar work is being conducted with other classes of compounds such as nitrogen heterocycles except in these cases zeolites and sodium acetate are being used to induce luminescence signals.

Analysis, continued

OHIO STATE UNIVERSITY
Columbus, Ohio 43210

419. DEVELOPMENT AND OPTIMIZATION OF METHODOLOGIES FOR ANALYSIS OF COMPLEX HYDROCARBON MIXTURES R. J. Laub Department of Chemistry	\$63,000	02-03
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The goals of this project comprise exploration and further clarification of optimization methodologies for gas- and liquid-chromatographic separation of complex hydrocarbon mixtures. Current attention is focussed on representation of chromatographic data via plots of relative retention as a function of the independent system variable(s) to be optimized. Techniques pertaining to routine fabrication of ultra-high efficiency g.c. and l.c. column systems of adjustable selectivity are being studied in order to provide as broad a range of boundary conditions as possible for the optimization strategies. A new separations method called rotating-disk thin-layer chromatography is being evaluated for pre-separation fractionation of complex samples such as crude oils. Kinetic band dispersion with each technique is being studied. Pseudo-mesogenic properties of thin films of g.c. stationary phases are being correlated with alteration of elution behavior of closely-related isomers and examined as a means of fine-tuning separations. Temperature effects and mobile-phase compositions are being optimized for microbore-packed l.c. columns.

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

420. QUANTITATION OF FOSSIL FUELS BY MASS SPECTROMETRY L. Wayne Sieck National Measurement Laboratory	\$110,000	02-03
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The goal of this project is to develop sub-minute mass spectrometric techniques for the screening and quantitation of fossil fuels and petroproducts which do not require prior fractionation or separation of the sample prior to the analysis. The basic method involves chemical ionization in which the solvents chosen for the fuel samples provide reagent ions which react with only certain components or classes of compounds. Alkanes, cyclohexane, chlorobenzene, and various alkyl benzenes have been found to be suitable solvents for generating charge exchange and/or proton abstraction (negative chemical ionization) spectra of various classes of substituted aromatics. Studies to determine ionization potentials of various target hydrocarbons via charge transfer equilibrium measurements, as well as the reactivity and selectivity of other reagent ions, are in progress.

Chemical Engineering Sciences

STANFORD UNIVERSITY
Stanford, California 94305

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|---|--------------------------------|-------|
| 421. TRANSPORT CHARACTERISTICS OF SLURRIES
IN PIPELINES: FLOW REGIMES AND PRESSURE
DROP | \$150,000
36 mo.
FY80-82 | 02-04 |
|---|--------------------------------|-------|
- Andreas Acrivos
Department of Chemical Engineering

This research aims to study the flow of slurries in pipelines from a fundamental point of view. Primary emphasis is placed on developing methods, based on sound scientific principles, for predicting the pressure drop and for delineating the various flow regimes that can occur in such systems. The theoretical framework is based on the equations of continuum mechanics and is being developed in close conjunction with a parallel experimental study. The conditions under which a settled suspension of coal particles in water can be resuspended in the presence of laminar shear flow are currently being investigated.

STATE UNIVERSITY OF NEW YORK/STONY BROOK
Stony Brook, New York 11794

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| 422. CHEMICAL REACTIONS AND TURBULENCE
Rene Chevray | \$49,972 | 02-04 |
|--|----------|-------|
- Department of Mechanical Engineering

High quality data are obtained for a well-defined turbulent situation - a two-dimensional mixing layer - with chemical reactions of known simple kinetics. Additional complexities of finite heat release are avoided by use of small concentrations for the reaction chosen ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* + \text{O}_2 \rightarrow \text{NO}_2 + h\nu + \text{O}_2$). Large Reynolds numbers, small dilution numbers, large reaction speed numbers and several concentration ratios are investigated. Conditional as well as usual measurements are made of separate and joint statistics of the velocity and concentrations fields obtained by laser doppler velocimetry and by absorption spectroscopy, respectively. On the theoretical front, the general problem of total dispersion of a scalar in turbulent flows is considered and a scheme is set up to model directly the equations describing the evolution of the probability density functions of the species concentrations in the free shear layer.

Chemical Engineering Sciences, continued

THE JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

423. PREDICTION OF THERMODYNAMIC PROPERTIES \$40,000 02-04
FOR COAL DERIVATIVES
Marc D. Donohue
Department of Chemical Engineering

The purpose of this project is to develop an engineering correlation to predict the thermodynamic properties of coal derivatives. The correlation is based on perturbed-hard-chain theory but includes additional terms for multipole interactions. The correlation allows prediction of vapor pressures, densities, enthalpies, heats of vaporization, 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 presently available. Experiments are now underway to measure Henry's Constants and infinite-dilute activity coefficients for intermediately sized hydrocarbons (e.g. nonane in methylnaphthalene). We are studying the differences among alkane-alkane, alkane-aromatic and aromatic-aromatic pairs.

UNIVERSITY OF CALIFORNIA/DAVIS
Davis, California 95616

424. STATISTICAL MODELING OF REACTING FLOWS IN \$64,954 02-04
TURBULENT AXISYMMETRIC JETS
H. A. Dwyer and W. Kollmann
Department of Mechanical Engineering

This program of research is concerned with the development of new and improved models of turbulence in variable density flows in general and turbulent flows with combustion in particular. The principle techniques which are being employed are: (1) Development and solution of probability density function equations (PDF) for scalar transport with chemical reaction; (2) Improved second order closure for Reynolds stress determination; and (3) Advanced sensitivity analysis to understand model function dependence and determine model constants. At the present time both the PDF and second order closure models are being applied to variable density shear flows with good success. Also, a complete sensitivity model is being completed for the popular $k-\epsilon$ model of turbulent flow, and important results on model constant sensitivity are being analyzed.

Chemical Engineering Sciences, continued

STANFORD UNIVERSITY
Stanford, California 94305

425. FUNDAMENTAL STUDIES OF FLUID MECHANICS AND HEAT TRANSPORT IN POROUS MEDIA	\$135,000 24 mo. FY81-82	02-04
George M. Homsy Department of Chemical Engineering		

Research under this contract is focused on understanding the flow of Newtonian and non-Newtonian fluids through porous media and the stability of processes which seek to produce oil by displacement with dilute polymer solutions. Recent work has included the exact calculation of the flow through and permeability of periodic arrays of particles. Our results for the permeability of such arrays cover the entire range of packing fractions, and agree well with previous limited numerical and asymptotic results. We have also investigated the theory of polymer flooding process which seek to stabilize a displacement which would be unstable if attempted with water alone. We have shown that if the total amount of polymer is fixed, there is an optimal manner in which to inject the material. We compute this optimal procedure and compare it with that used in practice. Some important aspects of the optimal procedure have not been previously explained or understood.

NATIONAL BUREAU OF STANDARDS
Washington, D. C. 20234

426. TRANSPORT AND PHASE EQUILIBRIA IN MULTICOMPONENT FLUIDS	\$65,000	02-04
John M. Kincaid Thermophysics Division		

The purpose of this project is to develop and implement simple, accurate techniques to treat the transport and phase transition properties of multicomponent systems. There are three basic aspects to the project: (1) the development of new techniques to study multicomponent systems; (2) the "translation" and adaptation of recent theoretical advances in transport and phase transition phenomena to forms usable to the energy technologies; (3) approximation assessment and implementation. All three of these areas can be expected to advance our understanding of multicomponent fluids at high temperatures. Recent progress includes: the development of a kinetic perturbation theory (1); the extension and elaboration of techniques used in polymer physics to the general problem of multicomponent phase equilibria (1); the calculation of multicomponent viscosity and diffusion coefficients for hard-sphere mixtures using the Revised Enskog theory (2); and molecular dynamics studies of diffusion in binary hard-sphere mixtures are being used to calibrate the RET (3).

Chemical Engineering Sciences, continued

NATIONAL BUREAU OF STANDARDS/BOULDER
Boulder, Colorado 80303

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| 427. INTEGRATED EXPERIMENTAL AND THEORETICAL
STUDY OF THE THERMOPHYSICAL PROPERTIES OF
FLUID MIXTURES
Neil A. Olien and Howard J. M. Hanley
Thermophysical Properties Division | \$125,000
15 mo.
FY80-81 | 02-04 |
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The program is a coordinated task of 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), to develop the theory of liquids and to develop models to predict the properties based on the theory and optimized by the data. A high temperature, high pressure PVT apparatus has been completed and will shortly be used to the PVT properties of H₂S. A vapor-liquid equilibria/liquid-liquid equilibria apparatus is under construction. Theoretical studies include computer simulation of fluids under shear. A computer package to predict the transport properties of hydrocarbons and their mixtures to C₂₀ has been completed.

NORTH CAROLINA STATE UNIVERSITY
Raleigh, North Carolina 27650

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| 428. DYNAMIC MEASUREMENTS OF TWO-PHASE FLOW
PHENOMENA USING NMR TECHNIQUES
R. F. Saxe
Department of Nuclear Engineering | \$64,000 | 02-04 |
|--|----------|-------|

This project involves the development of equipment and techniques to measure two-phase flow phenomena as a function of space and time utilizing NMR techniques. Repetitive scanning or Fourier transform techniques in the presence of a linear magnetic field gradient will be used. To date, most of the equipment has been designed, built and assembled and preliminary experiments suggest that an adequate signal/noise ratio is attained. The signals will be recorded as a time-series digitally on magnetic tape and subsequently analyzed by computer. The magnetic tape/computer system is now functioning successfully and the software needed is in place and checked. Initially, the system will be used on air/water mixtures either of known characteristics and/or measured also by, e.g., photographic techniques. The emphasis will be on proving the system's operation and on deriving the system's possibilities, limitations, accuracy and precision.

Chemical Engineering Sciences, continued

UNIVERSITY OF MINNESOTA
 Minneapolis, Minnesota 55455

429. FUNDAMENTAL HEAT TRANSFER PROCESSES \$59,675 02-04
 RELATED TO PHASE-CHANGE THERMAL STORAGE
 MEDIA
 E. M. Sparrow and J. W. Ramsey
 Department of Mechanical Engineering

This research program is focused on heat transfer which occurs in the storage of thermal energy by change of phase and encompasses studies of both melting and freezing. One of the freezing problems is concerned with the extent to which freezing can be enhanced by the attachment of fins to the external surface of a cooled vertical tube situated in a liquid medium. These enhancements tend to neutralize the degradation of freezing due to the thermal resistance of the frozen layer and to natural convection in the liquid phase. For freezing on an unfinned plane wall, it was found possible to obtain a closed-form analytical solution, while for freezing about a coolant-carrying circular tube, a new numerical methodology was devised. For melting, quantitative design-quality heat transfer coefficients are being determined experimentally for melting adjacent to a heated vertical tube. A dimensionless correlation enables these results to be used for a wide range of phase-change media. Melting of a phase-change material situated within a circular tube is being studied in connection with encapsulated storage systems.

STATE UNIVERSITY OF NEW YORK/STONY BROOK
 Stony Brook, New York 11794

430. TRANSPORT PROPERTIES OF MULTIPHASE \$145,000 02-04
 SYSTEMS 24 mo.
 George Stell FY81-82
 Department of Mechanical Engineering

General goals are a comprehensive microscopic theory of transport in two-phase random media and a comprehensive statistical mechanical theory of transport in fluids. New exact expressions for the n-point void probability functions characterizing microscopic structure of a two-phase medium are derived to obtain for a bed of impenetrable spheres strong bounds on the 3-point function as well as accurate evaluation of the 2-point function. Improved bounds on certain transport coefficients (e.g., conductivity) are also derived and evaluated for a bed of penetrable spheres, representing experimentally effective thermal-conductivity data of certain composite materials remarkably well. Transport coefficients for multicomponent systems in the revised Enskog theory (RET) are obtained and the RET embedded in a more general approximation scheme, describing particles with attractive interactions as well as repulsion. The result is used to obtain a molecular theory of intrinsic viscosities.

Chemical Engineering Sciences, continued

CORNELL UNIVERSITY
Ithaca, New York 14853

431. EXPERIMENTAL AND THEORETICAL STUDIES	\$163,643	02-04
OF DENSE FLUID MIXTURES	24 mo.	
W. B. Streett and K. E. Gubbins	FY80-81	
School of Chemical Engineering		

The fundamental goal of this research is to develop methods for correlating, extrapolating and predicting the physical and thermodynamic properties of dense fluids, by means of statistical mechanics and intermolecular potential theory. The research is part of a larger program that combines experiment, theory and computer simulation in a coordinated study of the thermodynamics of fluids. Experimental work under this project includes PVT measurements for pure fluids and mixtures at temperatures from 70 to 500 K and pressures to 1000 atmospheres. Theoretical work consists mainly of the application of statistical mechanical perturbation theory to the prediction of mixture properties.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

432. DYNAMICS OF VAPOR EXPLOSIONS	\$71,223	02-04
B. Sturtevant	20 mo.	
Graduate Aeronautical Laboratories	FY81-82	

The explosive vaporization of single droplets of volatile liquid heated to their limit of superheat is being studied for the purpose of understanding the rapid transport and dynamic processes which occur during the early stages of explosion when departures from thermodynamic equilibrium are very large. A series of single, short-exposure photographs and fast-response pressure measurements have been used to provide a description of the complete explosion process. An estimate of the evaporative flux into the single bubble observed in each exploding drop, calculated from the photographically-determined bubble growth rate and acoustic source strength from the pressure measurements, yields a value of $400 \text{ gm/cm}^2 \text{ sec}$, two orders of magnitude greater than that predicted by the classical diffusion-limited theory of bubble growth. The photographs show that such large rates are due to extreme roughening of the bubble surface, presumably due to a previously unobserved interfacial instability driven by rapid evaporation.

Basic Energy Sciences outlay funds 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.) Chemical Sciences FY 1981 Equipment Funds were assigned as follows.

	Equipment Funds <u>(K\$)</u>
Ames Laboratory	175
Argonne National Laboratory	750
Bartlesville Energy Technology Center	10
Brookhaven National Laboratory	900
Idaho National Engineering Laboratory	5
Lawrence Berkeley Laboratory	370
Lawrence Livermore National Laboratory	25
Los Alamos National Laboratory	55
Mound Facility	65
Notre Dame Radiation Laboratory	190
Oak Ridge National Laboratory	535
Pacific Northwest Laboratory	85
Pittsburgh Energy Technology Center	5
Sandia National Laboratories/Albuquerque	10
Sandia National Laboratories/Livermore	800
Solar Energy Research Institute	20

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