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Summaries of FY 1980 Research in the Chemical Sciences

September 1980

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

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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 for members of the scientific and technological public, and interested persons in the Legislative and Executive Branches of the Government, in order to indicate the areas of research supported by the Division and energy technologies which may be advanced by use of basic knowledge discovered in this program.

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 needs for knowledge among the developing energy technologies. For example, the potential benefits of unraveling the complexities of coal or sunlight-induced chemistry seem more applicable to this tax-supported program than adding fine points about the make-up of petroleum.

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.

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

Chemical Sciences Division
Office of Energy Research
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 is devoted to research in hot atom chemistry, the study of the effects of nuclear decay and the consequent release of energy on chemical reactions.

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 will be supported by this program when it opens in 1980. This laboratory will be a user facility in support of researchers from universities, industry and national laboratories and will offer use of advanced instrumentation to interested combustion scientists.

Atomic Physics (01-03)

The Atomic Physics Program supports basic research on phenomena dominated by the presence of atoms and their ions as distinct entities. 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 of magnitude at which energy, momentum and matter transfer occur. These studies require having available 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 involved 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 chemistry research which is related to chemical transformations or conversions which are fundamental to new or existing concepts of energy production and storage. Of particular interest, but not limited to, are those research activities with the objectives of understanding the chemical aspects of (1) catalysis, both heterogeneous and homogeneous, (2) the charaterization and transformation of fossil resources - particularly coal, (3) the conversion of biomass and related cellulosic wastes and (4) hydrogen production and storage. Aspects of 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 mateials 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 thermodynamics research on chemical and physical equilibrium, 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.

AMES LABORATORY
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A. J. Nozik - Phone: (FTS) 327-1953 or (303) 231-1953

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DOE Laboratories

Photochemical and Radiation Sciences

Chemical Physics

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Brookhaven National Laboratory

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Oak Ridge National Laboratory

Pacific Northwest Laboratory

Offsite Contracts

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 are given at the beginning of each such sequence.

There are two numbers above each summary, other than its ordinal number. The number immediately to the right of the name(s) of the investigator(s) indicates the scientific person years devoted to the project. The other number is the three digit code which identifies the DOE program which funds the project, as defined previously.

Photochemical and Radiation Sciences

Ames Laboratory Total $270,000
Iowa State University
Ames, Iowa 50011

1. PHOTOPHYSICS, PHOTOCHEMISTRY & SPECTROSCOPY 2.6 01-01
G. J. Small

This program is concerned with understanding how photons create excited vibronic states of organic molecules and the subsequent relaxation processes. The latter encompasses both photophysical and photochemical phenomena. Research in this field impacts a variety of others including organic pollutant detection and characterization and photosynthesis. Specific projects include: electronic energy transport in ordered and disordered solids with emphasis on the scattering processes which determine whether the transport is coherent or incoherent; two-photon absorption spectroscopy as a probe of the electronic and vibrational properties of molecules and solids; ultrafast photochemical rearrangement reactions as studied by hole burning spectroscopy; the formation of mixed exciton-photon states and their modification of the usual laws of light absorption; and the development of new laser based methodologies (e.g. nonphotochemical hole burning spectroscopy) for probing the structure of and light induced isomerization processes in amorphous solids (glasses).

2. PICOSECOND SPECTROSCOPY AND REACTION DYNAMICS 2.7 01-01
W. S. Struve

This program exploits picosecond laser spectroscopy to study dynamics of photochemical reactions. The emphasis of the program is to correlate ultrafast photoreactivity with excited state structure in molecules in which the latter is already comparatively well understood, and to evaluate the detailed effects of inert condensed media on photoreaction mechanisms. The chemical systems currently under study include diatomic halogens excited in RT solvents, 9-iodoanthracene, $Re_2Cl_8^{2-}$, $[W(Cp)(CO)_3]_2$, and transazobenzene. The experimental techniques currently used are time-resolved fluorescence, resonance Raman emission, and transient absorption spectroscopy, with Nd^{3+}:glass, high-repetition rate flashlamp-pumped tunable dye, and cw mode-locked dye lasers as excitation sources. A prime motivation of this research is to supply insights into molecular excited state processes pertinent to solar energy photocatalyst design.

Photochemical and Radiation Sciences

Chemistry Division Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439	Total $3,060,000

3. RADIATION CHEMISTRY OF LIQUIDS, SOLUTIONS AND ORGANIC COMPOUNDS G. Closs, C. Jonah, J. Miller, M. Sauer, S. Gordon, A. Trifunac, K. Schmidt	4.7	01-01

The goals of this research are the understanding of energy deposition of ionizing radiation in polar and non-polar liquids, and to gain an understanding of the structure of the primary species, especially in organic compounds. The reactive species produced by the primary events are used as reagents and probes to study electron transfer, redox processes, free radical reactions and excited states in organic and inorganic reactions. The process of energy deposition in fluids is being elucidated by studying solvation times and reaction rates of solvated electrons. Cyclopropenyl radicals are being generated by pulse radiolysis in a fundamental study of aromaticity. The yield of the hydrated electron and OH radical as a function of LET is being obtained. Pulse radiolysis is being used to study the redox and hydrolytic chemistry of actinides and lanthanides. The ANL pulsed electron linac and a 3 MeV Van der Graaff are the basic tools for all these experiments.

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

This program has as its objective the production of photosynthetic organisms substituted with rare, stable isotopes such as ^{2}H, ^{13}C, ^{15}N, ^{17}O, ^{18}O and ^{25}Mg. These organisms, as well as the pigments, proteins, lipids, and other components that can be isolated from them, are used extensively in research on photosynthesis. 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 of photosynthesis. 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.

5. GAS PHASE RADIATION CHEMISTRY RELEVANT TO COMBUSTION AND ATMOSPHERIC REACTIONS 3.2 01-01

S. Gordon, M. Sauer, C. Jonah,
W. Mulac

This research is directed toward an understanding of numerous fundamental reactions relevant to combustion and atmospheric processes and the temperature dependence of the combustion-related reaction kinetics at high temperatures. The experimental work includes the determination of the rate constants of reactions involving the OH, HO_2 and O radicals. The overall rate constant for HO_2 disappearance as a function of temperature and NH_3 or H_2O concentration is being analyzed in detail. The OH + HO_2 and O + HO_2 reactions are also being studied. With a high temperature cell, rate constant measurements for reactions up to 1000 K will be made. One factor in the dependence on temperature of OH reaction rates with substances such as H_2, CH_4 and CO is the specific vibrational rotational states of the OH radical as a function of temperature. We are looking at this dependence by exciting the OH radical into such specific states with a tunable narrow band pass laser and following the above reactions.

6. CHLOROPHYLL AND PHOTOSYNTHESIS RESEARCH 3.2 01-01

J. J. Katz, J. C. Hindman

Spectroscopic investigations on the chlorophylls are intended to provide a firm chemical and physical basis for the understanding of chlorophyll function in photosynthesis. Objectives are to characterize the excited state properties of chlorophyll systems, to elucidate the composition and structure of chlorophyll-chlorophyll and chlorophyll-ligand aggregates, and to make laboratory systems that mimic the essential features of *in vivo* photoreaction center and antenna chlorophyll. Current research falls into the following categories: (a) laser photochemistry and photophysics of chlorophyll systems, (b) structure of chlorophyll systems by nuclear magnetic resonance, with emphasis on the coordination behavior of chlorophyll, and by small-angle neutron scattering, (c) self-assembled and chemically-linked model systems, including linkage via the allomerization reaction, and (d) mass spectroscopy of chlorophyll aggregates, both hydrated and anhydrous.

Chemistry Division, ANL, continued

7. ELECTRON TRANSFER PROCESSES STUDIED BY RADIATION CHEMISTRY AND PHOTOCHEMISTRY 5.1 01-01
J. Miller, G. Closs, D. Meisel,
C. Jonah

The aim of this program is to study the fundamental processes associated with electron transfer to and from excited states, as well as thermally driven ground state reactions, with the ultimate goal of gaining an understanding of what governs efficient charge separation processes. One goal is to understand how electron transfer rates depend on energy, the molecular structure of the reactants, their orientations, and the distance between them. Kinetic pulse radiolysis is the tool of choice in these studies. Photochemical studies are aimed at achieving control of the microenvironment in which the photoredox reaction is driven in order to minimize back reaction. Micelles, polyelectrolytes and synthetic membranes are being used. Mechanisms of hydrogen production on gold sols from reactive intermediates are being evaluated using pulse radiolysis and isotope effect techniques. Photochemical charge transfer in hydroxylic solvents is being studied to attempt to minimize the back reaction by neutralizing (protonating or deprotonating) one of the charged photochemical products.

8. PHOTOSYNTHESIS STUDIES: REACTION CENTER STRUCTURES, FUNCTIONS AND MECHANISMS 4.9 01-01
J. Norris, G. Closs, L. Shipman, M.
Wasielewski, M. Thurnauer, M. Bowman

The fundamental goal of this program is to achieve a better understanding of the primary events of photosynthesis. The 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 including the two chlorophylls of the special pair; (c) identification of new long- and short-lived photoactive intermediates, particularly in green plants; (3) establishment of the kinetics of electron transfer in the initial chemical steps of photosynthesis; and (3) development of new theoretical insight to energy transduction and the structure of the photosynthetic machinery. The distance between Fe^{+2} and $(Bchl_2)^+$ in photosynthetic bacteria is being accurately measured by observing their magnetic interaction. Electron-nuclear double resonance and electron spin echo spectroscopy are being used to obtain additional structural and kinetic data. In addition, solid state NMR spectroscopy will be used as an exploratory probe of reaction center structure.

9. RADIATION AND PHOTOCHEMISTRY STUDIED BY MAGNETIC RESONANCE 4.9 01-01

A. D. Trifunac, G. Closs

This program aims at developing new magnetic resonance methods and applying them to problems in radiation and photochemistry. The methods are of broad scope involving electron and nuclear resonance of solids and liquids including optical detection. Chemically-induced dynamic nuclear polarization (CIDNP) involving both ^{1}H and ^{13}C in a flow system is being used to characterize radical reaction pathways via FT NMR analysis. Time resolved electron paramagnetic spin echo spectroscopy is being used in quantitative studies of radical kinetics, electron spin relaxation, and electron spin polarization in transient radicals. Micellar systems are being studied in order to elucidate the effect of order on charge separation processes. Fluorescence detection of electron spin resonance is being used as a probe in the recombination kinetics of radical ion pairs. A new solid state NMR spectrometer will be used as a probe of radiation damage in synthetic and biological 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. This work focuses on three interrelated facets of the problem. First, synthetic photoreaction centers are being prepared as biomimetic models of their natural counterparts. These systems include covalent chlorophyll trimers, chlorophyll-pheophorbide cyclophanes, and a four-body dimeric chlorophyll donor, two-chlorophyll acceptor system. Second, the photochemistry and electrochemistry of these models is being examined with respect to their ability to undergo light-induced electron transfer. The solvent has a marked effect on the back reaction of chlorophyll *a* cation radicals with either chlorophyll *a* or pheophytin *a* anion radicals. Third, a biomimetic device, the "synthetic leaf," designed to use these models for solar energy conversion is being developed. Present studies involve the use of semiconducting films of bis(Zn-chlorophyll) cyclophane deposited on platinum supports to photocatalyze the oxidation of hydroquinone to benzoquinone with red light.

Photochemical and Radiation Sciences

Chemistry Department Brookhaven National Laboratory Upton, New York 11973	Total $2,435,000

11. RADIATION CHEMISTRY B. H. J. Bielski, R. W. Dodson, R. A. Holroyd and H. A. Schwarz	6.0	01-01

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 nitrogen fixation.

This program aims 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 D. M. Brenner	3.2	01-01

The research program in laser-induced chemistry currently involves experiments related to the phenomenon of infrared multiphoton absorption and induced chemistry. Understanding the dynamics of absorption and probing the internal energy distribution of vibrationally-excited molecules prior to reaction are the objectives of these experiments. The latter require measurements involving energy transfer, spectroscopy, product analysis, opto-acoustic techniques; i.e., a wide range of methods is required to investigate the exceedingly complex nature of multiphoton-induced chemistry. The details of the energy transformation by which incident photon energy is converted into vibrational energy are being examined in the laboratory with several techniques including laser-induced fluorescence, photoionization, and infrared chemiluminescence.

13. PHOTOCHEMICAL ENERGY CONVERSION 6.7 01-01

C. Creutz, N. Sutin

This program involves photochemical investigations of transition metal complexes and, in particular, the electron-transfer properties of charge-transfer excited states exemplified by their reactions with inorganic oxidants and reductants in solution. Particular attention is being paid to systems capable of effecting the decomposition of water into hydrogen or other useful chemicals and oxygen. A major objective of this program is the quantitative study of the physical and chemical deactivation processes (luminescence, radiationless decay, and chemical "back-reactions") which can decrease light conversion and storage efficiencies; 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.

14. PICOSECOND SPECTROSCOPY 3.0 01-01

T. L. Netzel

Picosecond absorption and emission spectroscopies are employed to investigate the ultrafast unimolecular processes in complex molecular structures such as cofacial diphorphyrins, covalently linked two- and three-membered chlorophyll aggregates, and inorganic compounds with two metal nuclei. The scientific focus of this research program is on understanding photo-induced 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 M. D. Newton	3.0 1.5 1.0	01-01 01-02 02-01

The National Synchrotron Light Source now under construction at Brookhaven will provide high intensity, monochromatic photon beams ranging in energy from the ultraviolet to the x-ray region. An appreciable effort is now under way by members of the Chemistry Department to design, build, and eventually use facilities for 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. Most of the present efforts are being carried out in collaboration with university-based chemists who will form the nucleus of the outside user community at the synchrotron.

16. ENERGY TRANSFER IN CHEMICAL KINETICS R. E. Weston	2.6	01-01

Chemical reaction rates depend strongly on the distribution of reactant energy among translational, rotational, vibrational, and electronic degrees of freedom. Conversely, the energy distribution in reaction products can be used as a sensitive probe of the reaction mechanism. In either case, collisional energy transfer from excited atoms or molecules will perturb the energy distributions of reactants or products, and hence plays an important role in the reaction mechanism. Atoms or molecules are produced in specific excited states by a pulse of ultraviolet, visible, or infrared radiation and the transfer of both electronic and vibrational energy studied. The excited species can transfer energy to another molecule by collision, or can spontaneously lose energy by emission of fluorescence radiation at a rate determined by the natural lifetime of the excited species. The competition between energy transfer and emission leads to a decrease in observed fluorescence lifetime, which can be related to a bimolecular rate constant (and a cross section) for energy transfer.

Chemistry Department, BNL, continued

17. CHEMISTRY OF ENERGETIC ATOMS 7.5 01-01
A. P. Wolf and R. M. Lambrecht

This program is devoted to a study of the chemistry of energy-rich atomic and molecular species. These may be neutral or charged reactants in ground or electronically excited states, or reactants with high kinetic energies. Included are reactive intermediates produced by nuclear processes; reactions of C, N, O, and halogen atoms. Atomic species are also produced in known electronic states and with a known temperature by use of a microwave discharge. Spectroscopic techniques are used to identify reactants and products and to determine rates of gas phase reactions. Applications include: chemical reactivity and spin states of carbon, oxygen, and halogen atoms; the chemistry of fluorine atoms and fluorine molecules; chemical reactions of carbon and methyne ions. In addition, techniques for labeling compounds of medical, biological, and environmental interest are developed and the nuclear and chemical techniques are also being applied to chemical analysis of coal.

Photochemical and Radiation Sciences

Department of Energy and Environment — Total $845,000
Brookhaven National Laboratory
Upton, New York 11973

18. PORPHYRIN CHEMISTRY — 7.6 — 01-01

J. Fajer

This program encompasses synthetic, structural, theoretical and physical chemistry and addresses 1) the role of porphyrins in the transduction of light into chemical energy 2) the catalytic function of porphyrins in enzymatic reactions and 3) application of these reactions to biomimetic solar energy conversion, and photo-assisted catalytic systems for the fixation of carbon and nitrogen. Work in progress includes picosecond kinetics of electron transfer in cofacial porphyrins to model the reaction center for photosystem II (oxygen evolution in plant photosynthesis); rates of heterogeneous electron transfer between porphyrins and substrates; the role of isobacteriochlorin radicals in the conversion of nitrite to ammonia catalyzed by nitrite reductase; determinations, by x-ray diffraction, of the structures of methylbacteriopheophorbide, ytterbiumIIItetrapyridyl- and leadII ms tetrapropyl-porphyrins; EXAFS investigations of unusual oxidation states of metal porphyrins and of porphyrin radicals; and Pariser Parr Pople and extended Hückel theoretical calculations to guide the experimental investigations.

19. INVESTIGATION OF THE CHEMISTRY OF ENERGETIC COMPOUNDS — 3.0 — 01-01

Manny Hillman

This program is an investigation of the properties of compounds that have the ability to catalyze other reactions, the ability to become electrical conductors under the influence of light, and the ability to partake in chemical reactions under the influence of light. Various organometallic compounds are being investigated for these purposes using ferrocene as a model compound. The photoinduced conductivities of 2,4-dinitrophenylhydrazones of ketoferrocenes are being measured and correlated with structures. Compounds containing two metal atoms in close proximity are under study for both photoinduced conductivity and photoassisted chemical reactions. Of particular interest for the latter investigation is the decomposition of water. Compounds with large protruding and reactive orbitals are under consideration to study catalytic reactions such as the fixation of nitrogen.

20. KINETICS AND MECHANISMS OF CHEMICAL PROCESSES RELATED TO THE DEVELOPMENT AND USE OF ENERGY James W. Sutherland	3.0	01-01

The objective of this program is to develop basic kinetic and mechanistic information about selected chemical systems which are associated with the development and use of energy sources and for which present data are inadequate or unavailable. Short-lived transient chemical species are characterized by flash photolytic and pulse radiolytic techniques, while steady-state photolytic, steady-state radiolytic and standard kinetic methods are used to identify and measure yields of final products of a particular overall reaction. Principal topics being investigated are the photochemistry of selected molecules adsorbed on high surface area solids and the chemistry of transient nitrogen species. In particular, the influence of surface environment on modifying the photophysical and photochemical properties of pyrene adsorbed on porous glass is being studied. The chemistry of the transient species and permanent products formed in the photochemical and thermal reactions of hydrazine dissolved in acetonitrile are being investigated. Some aspects of the reactivity of sulphur dioxide are also being studied.

Photochemical and Radiation Sciences

Chemical Biodynamics Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	Total $415,000

21. ARTIFICIAL PHOTOSYNTHESIS 4.5 01-01
Melvin Calvin, J. W. Otvos,
W. E. Ford and I. Willner

The long-term goal of this project is the design and development of artificial systems that store solar energy by methods similar to those operative in green plant photosynthesis. Photosensitized electron transfer reactions across phase boundaries are being studied with the aim of stabilizing the primary photoproducts and preventing their back reaction. The energy thus stored will subsequently be channeled into the production of hydrogen and oxygen from water. The primary step of photosensitized energy storage has been demonstrated across the lipid bilayer wall of phospholipid vesicles as well as across the interface of water-in-oil emulsions. A detailed understanding is necessary of the mechanisms involved in these electron transfer reactions so that proper steps can be taken to improve efficiencies. As an aid to this end, flash photolysis studies are being started to observe and follow the fate of short lived chemical intermediates in the photosensitized reactions.

Photochemical and Radiation Sciences

Energy and Environment Division Lawrence Berkeley Laboratory University of California 94720	Total $130,000

22. PHOTOCHEMICAL CONVERSION OF SOLAR ENERGY L. Packer, A. T. Quintanilha, R. J. Mehlhorn	2.0	01-01

Our investigations of energy conversion by bacteriorhodopsin includes a broad attack on identifying structural features essential for the direct proton current generated by this photocatalyst. We use specific reagents developed by protein chemists, to modify aromatic amino acid residues (tryptophan and tyrosine), and positively (lysine, arginine) and negatively (glutamate, aspartate) charged amino residues in purple membranes and then correlate the affects with activity. Photocycle activity is measured by laser flash photolysis and resonance Raman techniques to detect intermediates; and related to light induced proton release and uptake (H+ electrodes) and surface electrical charge changes (flash EPR with spin probes). Deuterium isotope effects on these parameters of bacteriorhodopsin activity are also being investigated. This year the primary sequence of bacteriorhodopsin has been reported (Moscow, MIT), thus, chemical modification and labeling studies of these purple membranes should enable us now to arrive fairly rapidly at a clearer understanding of the basis of bacteriorhodopsin's photovoltaic effect.

Photochemical and Radiation Sciences

Materials and Molecular Research Division Total \$325,000
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

23. PHOTOCHEMISTRY OF MATERIALS IN THE STRATOSPHERE 3.0 01-01

H. S. Johnston

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. In one group of experiments, photochemical reactions are initiated by laser flash-photolysis, and the concentration of specific atomic or free-radical species, such as O, NO, Cl, and HO, is followed as a function of time by resonance fluorescence. This method is used to determine primary photolysis products, such as $NO_2 + O$ or $NO + O_2$ from NO_3 photolysis. In another group of experiments, photolysis is carried out by a sinusoidal light source, and kinetic information is obtained from the phase-shift of the observed products. The formation and reactions of the "free-radical reservoirs," N_2O_5, $HONO_2$, $HOONO_2$, are being studied, with especial interest to peroxy-nitric acid. As atmospheric scientists report measurements of stratospheric species, such as N_2O, HCl, CH_4, H_2O, NO_2, ClO, HOO, and O, these results are interpreted in terms of their contribution to the instantaneous global ozone balance.

24. PHOTON-ASSISTED SURFACE REACTIONS, MATERIALS AND MECHANISMS 1.6 01-01

G. A. Somorjai

This project explores photon-assisted chemical reactions that take place at the solid-vapor interface. These reactions include the photo-dissociation of water (H_2O) to produce hydrogen and oxygen and the photon-assisted reactions of carbon dioxide (CO_2) and water to produce simple hydrocarbons (photosynthesis). The purpose of these studies is to explore the mechanisms of photon-assisted surface reactions and then establish the optimum conditions (of surface structure, composition, temperature and reactant mixture) to maximize the rate of production of the desired chemicals (hydrogen and/or hydrocarbons).

Photochemical and Radiation Sciences

Notre Dame Radiation Laboratory University of Notre Dame Notre Dame, Indiana 46556	Total $2,035,000

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

The photochemical properties of transition metal ions complexed with macrocyclic ligands are being investigated. The effect of ligand structure, including the size of the macrocyclic ring, the extension of the π system and its overlap with the electronic density of the metal ion, is being examined using different members of a given family of macrocyclics. In addition, different metal centers with the same electronic structure are used in order to introduce variations in the photochemical responses of the complexes. Reference pulse radiolytic experiments are also being carried out to provide spectroscopic and reaction rate information on intermediates which are generated in redox reactions between radicals and inorganic systems. 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. The possibility of using copper complexes is particularly interesting since photosensitization with visible light by the metal center results in chemical changes in the macrocyclic ligand.

26. MICROWAVE STUDIES ON RADIATION INTERMEDIATES R. W. Fessenden	6.0	01-01

Methods involving the absorption of microwave energy are being used to study the geometric and electronic structure and reaction kinetics of transient radicals, ions, and excited electronic states produced by radiolysis and photolysis. Both resonant (ESR) and non-resonant (conductivity, dielectric loss) techniques are employed. Of particular note is a newly developed dielectric absorption method that is being used to examine the dipole moments and the reaction kinetics of photochemically produced triplet states. Microwave conductivity is being used to study electron attachment processes in gases at pressures of one atmosphere and above to determine the importance of Van der Waals complexes in these reactions and to examine ionization phenomena in dielectric liquids. Time-resolved ESR experiments provide information on the kinetics of specific radicals and on spin population dynamics. 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.

Notre Dame Radiation Laboratory, continued

27. THEORETICAL ASPECTS OF RADIATION CHEMISTRY K. Funabashi and A. Mozumder	3.0	01-01

Theoretical studies of the effects of the absorption of ionizing radiation in condensed systems are being carried out to provide a basic underlying structure for understanding radiation chemical experiments. Cross sections for capture of thermal electrons are being examined to determine thermalization times and distances. The influence of dielectric relaxation and field dependent transport coefficients on escape probabilities and on the ability of a reactive solute to trap electrons produced by ionizing radiation are being examined. A new model is being developed to describe the optical absorption spectrum and other physical properties of solvated and trapped electrons. Also under investigation are the consequences of relaxation and other effects at early times and the contributions of high energy secondary electrons to track processes, particularly as they affect radiolysis with heavy particles.

28. ELECTRICAL AND CHEMICAL PROPERTIES OF THIN FILMS W. H. Hamill and W. B. Berry	1.0	01-01

The phenomena associated with the injection, transport and trapping of very low energy excess electrons and holes in insulating liquids and disordered solids are being investigated. Topics under consideration include electron and hole injection, bond transport in crystals and certain liquids, hopping transport in most liquids, impurity and defect trapping and ion recombination. Consequences of the experimental observation that the rate of electron transport is proportional to the logarithm of time are being investigated. These studies, while motivated primarily by interests in the radiation physics and chemistry of low dielectric media, are of concern to electron transport in areas such as photosynthesis and ultimately to applied areas such as xerography and transmission line technology.

29. SPECTROSCOPY OF REACTION INTERMEDIATES J. Hardwick	4.0	01-01

High resolution spectroscopic studies of reactive species produced in radiolysis and photolysis are being carried out to identify those species, determine their molecular structures, probe their excited vibrational and electronic states, and determine the inter- and intramolecular pathways through which excess energy is redistributed. Laser excited resonance fluorescence is used, along with more conventional absorption and emission spectroscopy, to determine rotational, vibrational, and electronic energies with an accuracy limited only to the Doppler width of the spectroscopic lines. Radicals are also being studied in both the liquid and solid phase by resonance Raman techniques. In gas phase studies 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.

30. THEORETICAL STUDIES ON REACTING SYSTEMS J. J. Kozak and D. M. Chipman	4.0	01-01

New quantum mechanical methods are being used to provide information on electronic molecular structure of reactive intermediates and on the potential energy surfaces and reaction mechanisms involved in free radical reactions. A comprehensive theory of photo- and radiation- induced redox reactions in organized molecular assemblies is being developed. Statistical mechanical methods are being applied to examine the localization of energy and of reactive intermediates in organizates particularly with a view towards application to systems that may become important in the storage of solar energy. 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.

31. ELECTRON TRANSFER REACTIONS 5.5 01-01
P. Neta

Pulse radiolysis techniques are being used to characterize the kinetic properties and absorption spectra of short lived transient species produced by ionizing radiation. Approaches developed in this laboratory provide methods to examine 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 by kinetic spectrophotometric methods. 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.

32. INFLUENCE OF MOLECULAR ORGANIZATES ON CHEMICAL PROCESSES 4.0 01-01
L. K. Patterson

It is the purpose of these studies to develop basic information governing relationships between the organization of hydrophobically structured surfactant assemblies (monolayers, micelles, vesicles) and the influence these assemblies can have on the kinetics of bulk phase, interfacial and surface (two-dimensional) processes. Alterations in rates and reaction mechanisms as the result of surface orientation, reduction of dimensionality of the reactant phase, and compartmentalization of the reaction into microregions with well defined boundaries suggest the possibility for kinetic control over processes which is not possible in homogeneous solution. Such control has significant implication for concepts governing the design of systems appropriate to the chemical storage of energy. Techniques applied in these studies include chemical measurements, time resolved absorption spectroscopy and both steady state and time-resolved fluorescence spectroscopy. Studies being carried out in monolayers are particularly important in permitting control of the molecular organization.

33. RADIATION CHEMISTRY DATA CENTER 1.0 01-01

A. B. Ross

The Radiation Chemistry Data Center (RCDC) carries out a continuous survey of the literature of radiation chemistry and photochemistry, assembles appropriate bibliographic information on computer readable keyworded files, 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. These information services include keyword and author searches of its bibliographic files, searches of article titles for specific terms (character strings), preparation of current-awareness aids and bibliographies and compilation of specific data such as rate and spectroscopic information on reaction intermediates. 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.

34. CHEMICAL STUDIES OF RADIATION INDUCED REACTIONS 6.0 01-01

R. H. Schuler

Pulse radiolysis methods are being used to examine the production, optical spectra and reaction kinetics of reactive free radicals in aqueous solution and in hydrocarbons on the nanosecond and longer time scale. Results of direct time resolved measurements are correlated with those from more conventional analytical approaches, i.e. spectrophotometry and high pressure liquid chromatography, to provide a more complete picture of the overall mechanisms of radiation initiated reactions. Information derived from scavenging studies, both in pulse and in steady state experiments, is used to describe radiation produced events at times as short as 10^{-10} sec. Methods are being developed to use low Z ions having energies of 1-5 MeV/nucleon to provide a description of track effects in heavy ion radiation chemistry.

Notre Dame Radiation Laboratory, continued

35. ORGANIC PHOTOCHEMICAL PROCESSES 4.5 01-01

R. H. Schuler

Photochemical processes in organic systems are being examined to provide information on the role of intermediates including radicals, biradicals and triplet states, on the 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 biradicals, particularly those produced from aromatic ketones.

36. PHOTOISOMERIZATION 2.5 01-01

A. M. Trozzolo

Studies of the photo-induced ring opening of strained rings and photo-induced electron transfer reactions are being carried out. Included are the valence isomerism of heterocyclic compounds where the intermediate can be characterized and its chemistry can be studied, the electron transfer reactions of singlet oxygen, and the simulation of the transition-metal catalysis of ground-state reactions by photo-induced elecgron transfer reactions which produce similar products. In addition, we are looking at a number of adiabatic photo-chemical reactions which are quite novel since they produce excited-state products. The electron transfer reactions of singlet oxygen are being studied in view of the important role that this species plays in photooxidation and degradation of polymers and chemiluminescence.

37. ENERGY TRANSFER IN 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 tranfer in elementary processes. Interactions between metastable, excited rare-gas atom and various small molecules such as CO_2, H_2O, $(CH_2)_2O$, H_2, and F_2 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. Current emphasis is on potential energy surfaces of electronically excited rare-gas atom/molecular complexes, processes involving translational-to-rotational and translational-to-vibrational energy exchange, reactions of electronically excited neon and argon with water, and the mechanism of formation or rare gas/halogen exciplexes.

Photochemical and Radiation Sciences

Chemistry Division Oak Ridge National Laboratory P. O. Box X Oak Ridge, Tennessee 37830	Total $211,000

38. RADIATION CHEMISTRY AND PHOTOCHEMISTRY 2.0 01-01
C. J. Hochanadel, T. J. Sworski

The objective of this research is to obtain kinetic information that would allow meaningful modelling of combustion, coal conversion, atmospheric chemistry, solar energy conversion, or other systems of interest in the development and use of energy. The reactions studied most recently involved the free radicals CH_3, HCO, or HO_2. They were produced by the flash photolysis of H_2O vapor in the presence of CH_4, CO, or O_2, respectively. The reactions were observed by time resolved spectrophotometry. Numerical modelling was employed to fit theoretical curves to the data; kinetic parameters were adjusted by the method of least squares, and error limits were established by sensitivity analyses. Typical recent results were the important rate constants $k(HO_2 + OH) = (7.0 \pm 1.4) \times 10^{10}\ M^{-1}s^{-1}$, and $k(HO_2 + HO_2) = (4.0 \pm 0.7) \times 10^9\ M^{-1}s^{-1}$. Some new equipment, intended to provide improved versatility and accuracy, was installed and tested. This included a pulsed ultraviolet excimer laser, and a PDP 11/34 computer coupled with a Biomation wave form recorder for automatic data acquisition and processing.

Photochemical and Radiation Sciences

Research Division Solar Energy Research Institute 1536 Cole Boulevard Golden, Colorado 80401	Total $320,000

39. PHOTOCATALYSIS RESEARCH — 2.5 — 01-01
J. S. Connolly, J. C. Smart
and A. J. Frank
Chemical and Biological Division

The objectives of this program are to understand some of the molecular parameters required for efficient solar-induced photoredox processes. Studies include spectroscopy and photophysics of sensitizers, interfacial electron transfer, and synthesis of potential redox intermediates in photocatalysis. Structurally related porphyrinic molecules are being characterized by absorption and luminescence spectroscopy, fluorescence-lifetime measurements, and laser kinetic spectrophotometry. The emphasis in this area is on chlorins and bacteriochlorins, both natural and synthetic. Electrochemical and photoelectrochemical measurements are being performed on conductive membranes as a potential means of controlling the back reaction following light-induced charge separation. Synthesis, structure and reaction studies are being carried out on coordinatively unsaturated binuclear organometallic complexes as potential intermediates in redox catalysis. In addition, the spectroscopy and photophysics of these complexes are being investigated to understand the nature and fates of their low-lying excited electronic states.

40. BASIC STUDIES OF PHOTOELECTROCHEMICAL ENERGY CONVERSION — 0.8 — 01-01
A. J. Nozik, J. A. Turner
and J. Cooper
Chemical and Biological Division

Studies are being conducted on the basic nature of photoinduced charge transfer across semiconductor-electrolyte interfaces. A new mechanism is under investigation that involves charge injection into the electrolyte of photogenerated minority carriers that have not reached thermal equilibrium within the semiconductor space charge layer (hot carriers). Experiments are being done to test for hot electron injection from p-type semiconductors by probing reduction reactions having redox potentials above the conduction band edge (supra-band-edge reduction). With p-Si in non-aqueous electrolytes, supra-band-edge reductions are found but are explained by the unpinning of the semiconductor band edges at the electrolyte interface. This band-edge unpinning is caused by the creation of an inversion layer at the p-Si surface. Experiments are also being done to define the conditions required to generate ideal Mott-Schottky data. TiO_2 crystals can be treated to produce Mott-Schottky data showing perfect linearity, no frequency dispersion, and the theoretical pH dependence of the flat-band potential.

Chemical Physics

Ames Laboratory Iowa State University Ames, Iowa 50011	Total $540,000

41. STATISTICAL MECHANICS OF GASEOUS SYSTEMS 2.5 01-02
D. K. Hoffman

This work has two basic aspects. The first deals with the nonequilibrium features of surface adsorption-desorption mechanisms, x-ray damage and order-disorder rearrangement phenomena in crystals. The aim is to understand how the energetic and geometrical features of a surface or crystal serve to influence the distribution of irreversible events. For surface adsorption this is an important determinant of catalytic behavior. The general approach is to derive kinetic equations, based on an assumed irreversible mechanism, and to obtain solutions on a time scale for which equilibrium does not occur. A second aspect of this work is to understand transport and relaxation processes in polyatomic gases. An important feature of this program is to develop reliable collision models from which transport and relaxation cross sections which sensitively depend on inelastic collision mechanisms can be calculated quantitatively. The computational schemes under investigation attempt to exploit recent advances made in developing accurate approximation techniques for inelastic scattering problems.

42. ATOMIC MOLECULAR AND FREE RADICALS CROSSED BEAM KINETICS 2.5 01-02
C-y. Ng

This program emphasizes obtaining accurate and precise thermochemical data of concern in characterizing some elementary chemical reactions related to combustion. It combines the merits of the molecular beam method in the development of novel experimental approaches which make possible isolation and study of pertinent reactants and products. Ongoing projects at present include high resolution (3-meter VUV monochromator) studies of simple compounds such as NO, O_2, CO_2, COS, CS_2, SO_2, N_2O and NO_2. 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.

43. MOLECULAR BONDING THEORY 2.5 01-02

K. Ruedenberg, S. T. Elbert

Theoretical determination of molecular properties, geometric, electromagnetic and spectral, in particular of energy changes during chemical reactions, through quantum chemical calculations of electronic structures. Prediction of reaction energies and activation energies for elusive intermediates and transition states to contribute information which is needed in energy-related research, but difficult or impossible to obtain experimentally. Study of oxidation-reduction and exchange reactions involving carbon, nitrogen, oxygen and hydrogen to elucidate reactions occurring in combustion, in the atmosphere and in hydrogenations. Fundamental developments in beyond-Hartree-Fock many-electron quantum mechanics to achieve chemical accuracy by practical methods for predictions of reaction mechanisms. Analysis of electronic rearrangements along reaction paths and their energetic and kinetic implications to develop quantitative interpretative concepts for intuitive reasoning, consistent with ab-initio calculations, so as to anticipate energetic consequences of reactive changes with minimal computation.

44. MASS SPECTROMETRY-ION SOURCE CHEMISTRY 1.5 01-02

H. J. Svec and G. D. Flesch

This program emphasizes studies of the production of gaseous ions and neutral products resulting when molecules interact with energetic electrons. When the tetramethyl derivatives of silane, germane, stannane, and plumbane dissociate as a result of such interactions, methyl radicals and Si^0, Ge^0, Sn^0, and Pb^0 atoms are produced. The methyl radicals are vibrationally excited and the atomic species are formed in an autoionizing state as well as their ground electronic state. In the case of tetramethyl methane (neopentane) the neutral products are not clearly delineated because of ambiguities in the experimental measurements. The development of a double-ended neutral fragment mass spectrometer, ultimately capable of coincidence measurements of ions and complementary neutral species, is far enough along now to predict positive prognosis for alleviating such ambiguities. Highly excited carbon atoms may play a role in the formation of soot when hydrocarbons burn and highly excited lead atoms may play a role in the poisoning of catalysts in automotive exhaust systems when leaded gasoline is used.

Chemical Physics

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

Total $1,125,000

45. HIGH-RESOLUTION SPECTROSCOPY 3.2 01-02
H. M. Crosswhite, F. S. Tomkins,
K. T. Lu

This work focuses on (1) the influence of applied electric and magnetic fields on atomic spectra, (2) the study of the importance of weak, long-range atom-atom or molecule-atom forces for collisional effects, and (3) the development of vacuum ultraviolet tunable lasers. Rydberg spectra calculations of diamagnetic effects in lithium and sodium vapor, including allowance for the motional Stark effect, are being made which are in excellent agreement with experimental spectra to $n = 30$. Stark-effect spectrograms of the ^2P sodium Rydberg series are being taken in preparation for experiments with crossed electric and magnetic fields. Pressure effects on non-Rydberg atoms are also being studied, and europium vapor and other complex vapor spectra are being recorded. Coherent light generation in the vacuum ultraviolet is being studied via four-wave mixing in beryllium vapor. A theoretical search, concentrating on anti-Stokes Raman processes, for alternatives to the beryllium experiments is also being conducted.

46. THEORETICAL CHEMISTRY 4.7 01-02
T. H. Dunning, Jr., G. P. Das, L. B.
Harding, L. L. Shipman, A. F. Wagner

The theoretical chemistry program is a wide-ranging activity, emphasizing studies of reactions of importance in combustion as well as studies of the chemistry of metal atom clusters and of the molecular aspects of photosynthesis. Combustion chemistry. This activity focuses on *ab initio* calculations of the energetics and dynamics of reactions involved in the oxidation of hydrogen and simple hydrocarbons (methane, acetylene, ethylene). Cluster chemistry. This activity is concerned with the theoretical characterization of molecular species containing transition metal atoms and of clusters of transition metal atoms and chemisorption and reactions thereon. Photosynthesis. This activity focuses on the application of theories of light absorption, energy transfer and energy trapping by systems of interacting chromophores to the problems involved in solar energy conversion in natural and artificial systems. The development of computer software for chemical computations is also an important activity of the group.

47. MOLECULAR SPECTROSCOPY 0.6 01-02
J. R. Ferraro

This program involves the synthesis and characterization of new electrical conductors. The areas of ionic-, one-dimensional, super- and semiconductors are under study. One-dimensional, linear chain Pt and Pd complexes with macrocyclic ligands and the tri-iodide ion are being used to elucidate conductive mechanisms. These complexes are distorted and non-planar. Numerous new solid electrolyte ionic conductors are being synthesized. These conductors are substituted pyridinium and quinolinium organic ammonium silver iodides that show superior light and temperature stability. High temperature and pressure produce new conducting phases of these materials.

48. CHEMISTRY OF THE MHD PROCESS 1.0 01-02
J. C. Hindman

The goal of this project is to determine and monitor those fundamental factors which influence electron density and mobility in a coal-fired plasma. We are examining laser spectroscopic methods as nonintrusive probes for combustion systems. Coherent anti-Stokes (CARS) spectroscopy is, in principle, ideal for the determination of plasma species and their vibrational and rotational properties. Studies of NO_2 show that the CARS signal is quenched by various molecular species at low pressures. The CARS technique is now being applied to such radicals as OH, CN and C_2. Also, we are investigating methods that permit introduction of potassium vapor directly into the combustion plasma of a sheathed burner. This technique allows direct study of reactions of thermally-excited stable plasma species, as H_2O, CO_2, O_2, CO and N_2, with potassium.

49. MOLECULAR BEAM AND METAL CLUSTER CHEMISTRY RESEARCH 3.2 01-02
S. Wexler, E. K. Parks, T. H. Dunning, Jr.

Over the past several years, a unique crossed-molecular beam facility has been devoted to the study of chemical reactions at hyperthermal energies (from thermal to 350 eV). The facility yields fundamental information on the dynamics and energetics of (1) chemi-ionization reactions of actinides and lanthanides, (2) electron transfer reactions of alkali atoms with O_2, halogens, and metal hexafluoride molecules, and (3) collision-induced dissociation to ion pairs. Accurate absolute cross sections are determined. An important objective is the understanding of the fundamental factors which regulate the formation and breakup of chemical bonds. In addition, a multi-expansion cluster source is being used to generate beams of clusters of catalytically active metal atoms, e.g. Ni, in order to determine their size distributions, ionization potentials, electron affinities, electronic spectra, and structures. Cluster beams of other refractory metals such as Au are also being generated and studied.

Chemical Physics

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

Total $2,840,000

50. NEUTRON SCATTERING AND MOLECULAR STRUCTURE AND DYNAMICS 7.0 01-02
H. J. Bernstein, L. M. Corliss,
J. M. Hastings, T. F. Koetzle,
R. K. McMullan and R. Thomas

The structural program emphasizes crystal structures where hydrogen atoms are important, structures containing magnetic ions, and disordered or partially-ordered structures. Examples of systems being studied include organometallic substances, transition-metal hydrides and hydride coordination compounds, ionic conductors, magnetic compounds, and organic crystals. Studies combining x-ray and neutron diffraction are undertaken to examine molecular charge-density distributions. Measurement of both the energy and momentum changes undergone by neutrons on scattering is used to study atomic motions in solids. In magnetic systems the spatial distribution of magnetization and the behavior of spontaneous fluctuations are measured, both of which are essential to understanding magnetic phase diagrams, their associated first- and second-order transitions, and multicritical points where lines of transitions intersect.

51. HIGH FLUX BEAM REACTOR OPERATION --- 01-02
L. M. Corliss, J. M. Hastings
and T. F. Koetzle

The High Flux Beam Reactor provides an intense, steady-state source of thermal neutrons used in a variety of experiments by members of the Chemistry, Physics, and Biology Departments at Brookhaven and by outside groups as well. The nine beam ports are currently outfitted with twelve experimental facilities. Chemistry and Solid State Physics have a program for the joint use of these facilities. These include both elastic and inelastic neutron scattering spectrometers. The Chemistry effort is concentrated in areas of structural studies, magnetic phase transitions, and critical phenomena.

52. THEORETICAL CHEMISTRY S. Ehrenson, J. T. Muckerman and M. D. Newton	5.5	01-02

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 in the gas phase and in condensed phases, 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.

53. ION-MOLECULE REACTIONS L. Friedman and R. J. Beuhler	6.0	01-02

Mass spectrometry of molecular species having m/e values well in excess of 1000, up to and including m/e values approaching 10^6, is a major goal of this research program. Energy transfer in collisions of gaseous ions on solid surfaces has been studied extensively to provide the foundation required to develop sensitive single ion detection techniques for macromolecular weight ions. Ion source techniques with aerosol ion sources, ultra-rapid heating of solid surface sample probes, etc. are a major subject of investigation with the view to development of an integrated experimental system that will extend the capabilities of structural and analytical mass spectrometry to small macromolecules as well as fragile inorganic and organic molecular systems.

54. MOLECULAR BEAM STUDIES 2.0 01-02
J. R. Grover

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 utilizing the tunable vacuum ultraviolet radiation for photoionization. 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. A second project uses a crossed molecular beam technique having one of the reagent beams labeled with a short-lived ($\lesssim 10^{-1}$ sec) radioactive isotope to measure absolute differential cross sections for reactive scattering.

Chemical Physics

Department of Energy and Environment Total $440,000
Brookhaven National Laboratory
Upton, New York 11973

55. BIOELECTROCHEMISTRY 3.0 01-02
S. Feldberg

The fundamental goal of this project is to understand the mechanisms by which charge (ions and/or electrons) can move across bilayer lipid membranes. These studies are relevant to the role of organized structures in the conversion of light energy to chemical energy as well as to fundamental charge transport and energy transport phenomena in biological systems. Magnesium etiochlorin (Mg-C) incorporated in a bilayer lipid membrane separating aqueous phases containing ferri and ferrocyanide facilitates electron translocation across the membrane more effectively than any previously reported system. Electrical studies on planar bilayers are augmented by optical studies using vesicles. The immediate objective is to establish the mechanism by which this electron translocation occurs.

56. KINETICS AND MECHANISMS OF ALTERNATIVE FUELS COMBUSTION 3.9 01-02
R. Bruce Klemm

The objective of this task is to investigate the chemical kinetic and mechanistic factors involved in gas phase combustion and pollutant formation processes. Particular emphasis is placed on alternative fuels which comprise a wide range of fuel types, including methyl and ethyl alcohol, synthetic hydrocarbons, and hydrogen. There is an additional long range and fundamental interest in the effects of combustor operating conditions and fuel parameters on the mechanisms of combustion, such as pollutant emission rates and combustion efficiency. Two complementary techniques are utilized in determining specific rates for combustion related, elementary atom-molecule reactions. Combined, these experimental methods provide an unusually wide temperature span, ∿ 200-1200K, over which direct kinetic studies of combustion initiation reactions and oxidation reactions of combustion intermediates may be made. In addition, a photo-ionization mass spectrometer (PIMS) experiment that utilizes the National Synchrotron Light Source is being developed jointly between the Dept. of Energy and Environment and the Chemistry Dept.

Chemical Physics

Energy and Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	Total $65,000

57. UNIMOLECULAR KINETICS N. J. Brown	1.5	01-02

This proposed research is concerned with formally extending unimolecular rate theory and applying the theory to important combustion reactions. Unimolecular reactions play a crucial role in combustion initiation, fuel pyrolysis, radical quenching, and pollutant formation and destruction mechanisms. This fiscal year, research has focused upon acquiring an improved description of small molecule dissociation reactions which includes conservation of angular momentum. Calculations of rate coefficients for specific reactions will be obtained over a variety of conditions. A dynamical study of intramolecular energy transfer is underway to determine whether or not HO_2 dissociation near the high pressure limit is consistent with the random lifetime approximation.

Chemical Physics

Materials and Molecular Research Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	Total $1,838,000

58. ENERGY TRANSFER AND STRUCTURAL STUDIES OF MOLECULES ON SURFACES C. B. Harris	2.4	01-02

The purpose of this research program is to develop new 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 and the resulting product distributions, and (c) the study of the vibrational structure of molecules adsorbed on metal surfaces via Laser Raman Scattering. An additional goal of the research is to study the dynamics of energy transfer from adsorbed molecules to metal surface as a function of both the character of the molecules and their interaction with the metal surface as well as the distance away from the surface.

59. CROSSED MOLECULAR BEAMS Y. T. Lee	3.7	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.

60. CHEMICAL DYNAMICS STUDIES 2.0 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 non-reactive 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 inducted fluorescence has been constructed and operated successfully.

61. THEORY OF ATOMIC AND MOLECULAR COLLISION PROCESSES 1.4 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.

62. SELECTIVE PHOTOCHEMISTRY 1.0 01-02
C. B. Moore

The fundamental goals of this project are to understand the photophysics of selective excitation of molecules, the dynamics of energy transfer and specificity loss, and the chemical reactions of specifically excited states. Vibrational energy transfer for matrix isolated molecules and for chemisorbed molecules in catalytically important systems are being studied. The nature of highly vibrationally excited species is proved using both Fourier transform infrared spectroscopy and laser optoacoustic spectroscopy. Studies of the unimolecular decomposition of these vibrationally excited species following state selective excitiation are in progress. Excitation of a mode close to the reaction coordinate may greatly enhance the yield of selected products. Radical chemistry and the phtochemistry of small polyatomics are investigated following laser flash photolysis. The dissociation photoionization of liquid water with infrared and visible photons is also studied.

63. PHYSICAL CHEMISTRY WITH EMPHASIS ON THERMODYNAMIC PROPERTIES 2.7 01-02
K. S. Pitzer

One important set of objectives includes the development of a quantum chemistry for heavy atoms where relativisitic effects are important and the prediction of numerous properties of molecules containing such heavy atoms. Effective potential methods are used. The major relativistic effects, which arise for electrons near the nucleus, are incorporated into the effective potentials which then reflect these indirect effects on the valence electrons and their capacity to form chemical bonds. 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 goethermal 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.

64. POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS 1.6 01-02
H. F. Schaefer, III

This research project has two goals. The first goal is the development of new theoretical and/or computational methods for the description of "what electrons are doing in molecules." The second goal of the research is to apply these theoretical methods to significant problems of broad chemical interest. Currently, two areas are of dominant interest: (1) model theoretical studies of chemisorption, metal clusters and catalysis, and (2) the potential energy surfaces which govern gas-phase chemical reactions. Research in the former area is aimed at a truly molecular understanding of catalysis. In the latter area, research often tends toward molecules potentially important in the development of high powered laser systems.

65. PHOTOELECTRON SPECTROSCOPY 6.3 01-02
D. A. Shirley

Electron spectroscopy; electronic structure of matter, as determined through binding-energy measurements. Structures of high-temperature species and their interactions with radiation and surfaces, properties of both clean surfaces and adsorbate-bonded surfaces, energy transfer and lifetimes in high-energy eximers, and electronic structure of Van der Waals' molecules. Development of new electron spectroscopic techniques and synchrotron radiation applications, including extended X-ray absorption fine structure (EXAFS) at low photon energies.

66. MOLECULAR BEAM SPECTROSCOPY 1.0 01-02
J. S. Winn

This project derives fundamental information on molecular structure and the dynamics of energy disposal in molecular collisions through the use of several spectroscopic techniques. Molecular and metallic clusters are of particular interest. A variety of methods are being developed to produce free metal atoms, metal clusters, and thin metal films starting from volatile organometallics or metal carbonyls. The dynamics of collisional electronic energy transfer, the products of photolysis, and the generation of metal clusters from supersonic molecular beam expansions are being investigated. The structures and detailed intermolecular potential energy surfaces are analyzed by molecular beam electric resonance spectroscopy and by various potential inversion methods. Emphasis is placed on the rare gas halides and rare gas halogen weakly bound species.

CHEMICAL PHYSICS

NATIONAL RESOURCE FOR COMPUTATION IN CHEMISTRY LAWRENCE BERKELEY LABORATORY UNIVERSITY OF CALIFORNIA Berkeley, California 94720	Total $922,000

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

The NRCC established a software library and software distribution system with state-of-the-art holdings in the principal areas of computational chemistry including chemical kinetics, crystallography, macromolecular science, physical organic chemistry, quantum chemistry, and statistical mechanics. Six workshops and symposia were organized in these areas - two resulting in the creation of new computer software with capabilities exceeding software presently available in quantum inelastic scattering and multiple isomorphous replacement. A working group of quantum chemists, collision theorists, and other theorists from DOE laboratories and universities was organized to pursue a joint theoretical effort on the chemistry of combustion. The initial focus is the computation of potential energy surfaces for the simplest reactions persumed to be important in combustion.

Chemical Physics

Chemistry Division Oak Ridge National Laboratory P. O. Box X Oak Ridge, Tennessee 37830	Total $800,000

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

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 being carried out as a function of photon energy with emphasis on the use of synchrotron radiation. Results are being obtained on partial cross sections, angular parameters, autoionization, 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 means for using ARPES in the determination of the nature of surface adsorption of molecules. Most significantly, the measurements of the partial and differential cross sections as a function of photon energy will enormously enlarge the capabilities of photoelectron spectroscopy by examining the detailed nature of molecular wave functions as well as the ionization potentials, thereby providing the best and most comprehensive experimental basis for understanding molecular orbital theory.

69. THEORETICAL CHEMISTRY 1.0 01-02
O. H. Crawford

This program contributes to a fundamental understanding of atomic and molecular dynamics through the development of appropriate quantum and classical mechanical theories. Problems relevant to DOE interests are chosen for study from a range of subject areas including interactions of energetic particles and ions with solids and processes of laser chemistry. For example, a theory is being developed for the estimation of rates of energy loss of swift ions (from an accelerator) moving in crystalline channels. These values are needed for the extraction of depth profiles of crystal dopants from ion scattering data. Another area of investigation is the vibrational relaxation of isolated polyatomic molecules, which is important for laser chemistry.

Chemistry Division, ORNL, continued

70. 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 and MHD plasmas. 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.

71. PHOTOCHEMICAL, PYROLYTIC AND REACTIVE INTERMEDIATES BY ELECTRON SPIN RESONANCE 2.0 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 600°C and pressures to 2000 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 cumene, ethylbenzene, and t-butylbenzene. 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 Laboratories-Livermore
Livermore, California 94550

Total $2,000,000

72. COMBUSTION ANALYSIS BY ADVANCED METHODS 12.0 01-02
M. A. Gusinow and D. R. Hardesty

The primary goal of the present research is the utilization of laser spectroscopic techniques for studying the chemistry of combustion-related reacting systems with special emphasis on soot formation mechanisms, nitrogen chemistry, and turbulent combustion. Measurements of minor species by Raman scattering, laser induced fluorescence, and laser absorption are being conducted to elucidate pertinent radical chemistry (e.g., OH, CH, and NH_2). A slow-flow reactor is being used to study radicals important in hydrocarbon chemistry. Detailed mechanistic studies utilize laser photolysis and laser induced fluorescence to isolate important species. Detailed modeling of the $NH_3/O_2/NO$ system is ongoing and is being compared to experiment. A considerable emphasis is being given to turbulent diffusion flame studies and the measurement of mean and fluctuating values of velocity, temperature, and major species concentrations. The techniques being used are Rayleigh and Raman scattering along with two-component laser velocimetry.

73. COMBUSTION DIAGNOSTICS RESEARCH 6.0 01-02
M. A. Gusinow and P. L. Mattern

This work emphasizes the development of new techniques and the application of more classical approaches, such as spontaneous Raman scattering and analytical spectroscopy, for the study of combustion. The present studies are concerned with evaluating the utility of techniques such as polarization CARS, stimulated Raman, and inverse Raman spectroscopy to the measurement of primary and trace species in reacting systems. Basic studies (both experimental and theoretical) are being conducted on line-broadening mechanisms and the effect of rotation-vibration interaction on line intensities for Raman and fluorescence spectroscopy. Because of the importance of radical chemistry, experiments are being conducted utilizing time-resolved mass spectrometry coupled with laser pumping of specific reactants.

74. CRF PLANNING, DEVELOPMENT AND OPERATION 8.0 01-02
J. E. Marion and R. H. Johnsen

This activity includes the planning, developing and operation of the Combustion Research Facility at Sandia in Livermore. The present effort is focused on managing completion of the construction project, conducting initial occupancy, developing the necessary diagnostic and support equipment and describing the procedures for user access. The facility opens in late FY80 and will provide state-of-the-art combustion research laboratories to outside users. Combustion diagnostics will be emphasized and a wide range of laser capabilities will be available. In addition, CRF will contain advanced burner facilities and other combustion devices plus access to Sandia's CRAY computer to allow for a strong interaction between experiment and modeling. CRF will also conduct in-house combustion research that will complement and interact with user activities.

Atomic Physics

Physics Division Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439	Total $1,480,000

75. PHOTOIONIZATION-PHOTOELECTRON RESEARCH J. Berkowitz and J. H. D. Eland	2.9	01-03

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. The studies involve fixed and variable wavelength photoelectron spectroscopy, photoionization mass spectrometry and photoion-photoelectron coincidence spectroscopy. This past year a much better understanding has been gained of the photoionization of open-shell atoms by obtaining a photoelectron spectrum of atomic iodine. There has been success in quantitatively interpreting the partial cross sections observed, as well as earlier data on atomic chlorine and bromine, by utilizing an irreducible tensor angular momentum coupling scheme. This scheme is currently being tested on other atomic configurations to see if it has general application. Complementary studies are in progress on the variable wavelength photoionization spectra of atomic iodine and atomic tellurium. Photoionization mass spectrometry has been applied to determine the variation of ionization potential with cluster size for alkali halide monomers, dimers and trimers.

76. BEAM-FOIL RESEARCH AND COLLISION DYNAMICS OF HEAVY IONS H. G. Berry	5.4	01-03

The work in atomic structure using fast ion beams is aimed principally at improving the understanding of relativistic and quantum electrodynamic effects in heavy ions. Systems with only a few (1—4) electrons are studied to test precise ab initio calculations and many-electron systems to test more general relativistic calculations (e.g., relativistic Hartree-Fock). In atomic collision studies, the alignment and orientation production of excited states in fast ion-solid interactions are analyzed. Total excitation probabilities are also measured and studied in terms of secondary electron production and molecular coherence effects. Charge changing cross sections of slow Xe^+ ion beams (25—150 keV) are also being studied as part of the ion fusion research program (Accelerator Research Facilities Division).

77. HIGH-RESOLUTION LASER-RF SPECTROSCOPY WITH ATOMIC AND MOLECULAR BEAMS 3.5 01-03

W. J. Childs, L. S. Goodman, S. A. Lee

The atomic-beam apparatus that is used for laser-fluorescence studies and ultrahigh-precision laser-rf double-resonance atomic spectroscopy (of ^{138}La and ^{141}Pr in CY 1979) has also been employed to study the CaF molecule. The information obtained about the energy levels of the $^2\Sigma_{1/2}$ electronic ground state of this molecule is, both in precision and scope, a major qualitative advance in this field of research. Interesting applications of this now demonstrated technique are contemplated for experiments of interest in astrophysics and molecular structure. The CaF experiments would hardly have been possible without a wavelength meter built in this laboratory. This is a dual-path Michelson interferometer that allows high-precision measurement of a dye-laser-light wavelength relative to the wavelength of light from a He-Ne standard laser. The efficiency of running and analyzing experiments and the quality of the data taken is being improved with the use of a PDP-11/V03 computer for data handling and experiment management.

78. DISSOCIATION AND OTHER INTERACTIONS OF ENERGETIC MOLECULAR IONS IN SOLID AND GASEOUS TARGETS 6.9 01-03

D. S. Gemmell

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 has recently been modified to permit the detection of fragments in coincidence. The work has two main objectives: (a) a general study of the interactions of fast charged particles with matter, but with the 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 progress through the target) and (b) a study of the structures of 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 offer exciting possibilities as a new method for determining molecular-ion structures.

79. INTERACTION OF ENERGETIC PARTICLES WITH SOLIDS 1.2 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.

80. MOSSBAUER EFFECT RESEARCH 1.1 01-03

G. J. Perlow

A major effort has been devoted to experiment and theory concerning quantum beats of recoil-free γ rays. They are an interference phenomenon among the energy components of the radiation-field amplitude produced by frequency modulation of a Mössbauer source. The interference exactly vanishes except if the radiation passes through a resonant absorber which alters the phase and amplitude of one or more of the components. It is manifested in a time spectrum of the counting rate of the transmitted radiation. A harmonic analysis of the time spectrum shows the harmonic amplitudes to be very sensitive to small energy shifts between source and absorber. This has been tested by measurement of the relativistic second-order Doppler shift in a resonant absorber whose temperature is varied. One may readily observe shifts corresponding to changes of only 2°K in temperature. A theory of the process has been made using the optical theory of the resonant media. It describes both the beats and an interesting dispersion phenomenon seen when Mössbauer velocity spectra are taken with counts received during some restricted phase interval of the modulation cycle.

Atomic Physics

Physics Department Brookhaven National Laboratory Upton, New York 11973	Total $104,000

81. ATOMIC PHYSICS RESEARCH K. W. Jones	2.4	01-03

A variety of heavy ion beams, with energies in the range 20-250 MeV, from the Brookhaven Tandem Van de Graaff Facility are used for experiments in beam-foil spectroscopy, x-ray production in heavy ion-atom collisions, electron-heavy ion excitation and ionization cross sections. Beam-foil experiments concentrate on measurements of the charge state dependence of spectra in the region from 5-50 nm for elements such as Ti, Fe, and Mo and on lifetimes of resonance transitions in the Be-, Na-, Cu-, and Zn-like sequences. 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 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. Results obtained should be useful for the design of Tokamak fusion devices and in the interpretation of the radiation observed from them, as well as for the development of atomic theory. 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 $397,000

82. ATOMIC PHYSICS R. Marrus	6.8	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 relativisitic 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 Scientific Laboratory
University of California
P. O. Box 1663
Los Alamos, New Mexico 87545

Total $79,000

83. THE HIGH DENSITY OF Z-PINCH DIAGNOSTICS AND ATOMIC PHYSICS 1.0 01-03
L. A. Jones and D. B. Thomson

The purpose of this program is to understand the atomic and plasma physics which occurs in a hot dense plasma. The plasma produced ($Ne \simeq 10^{20}$ cm^{-3}, $Te \simeq 100eV$) is generated when the focussed beam of a laser initiates a small ($\sim$ .3 mm diameter) current carrying channel in a high pressure gas (1 - 5 atm. H_2). The current which ohmically heats the plasma column is provided by a Marx bank-water line combination which can provide over 0.8 Meg Amps of current in about 200 ns. This experiment has been operated at two different bank charging voltages and it is found that the two conditions give results which indicate that different processes dominate the plasma formation. A comparison with a calculation suggests that more material is accrued into the discharge column than classical theory would predict and our short term goal is to determine which processes are non classical and by how much.

Atomic Physics

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

Total $805,000

84. COLLISIONS OF LOW ENERGY MULTICHARGED IONS

1.0 01-03

C. F. Barnett and D. H. Crandall

This experimental program concentrates on atomic collisions involving multicharged ions at low energy. Total cross sections for electron capture from neutral atoms (primarily atomic hydrogen) by the multicharged ions are measured at velocities below the oribital velocities of the electrons with emphasis on attaining very low collision energies. Cross sections for electron impact excitation and ionization of a few multicharged ions are being measured with crossed electron and ion beams for energies near the ionization and excitation thresholds. Current investigations of electron impact processes reveal the importance of inner-shell excitation followed by autoionization to the total ionization cross sections as well as provide benchmark tests of developing theory.

85. THEORETICAL ATOMIC PHYSICS

1.0 01-03

R. L. Becker

Detailed calculations are being made for atomic collision processes. Experiments at ORNL have prompted two theoretical approaches to ion-Rydberg atom ionization theory. The capability of preparing Rydberg atoms in (n,ℓ)-selected states by laser excitation has motivated an extension of binary encounter and of classical trajectory Monte Carlo theory to treat initial states of specific angular momentum, ℓ. The theory gives good agreement with the ℓ-changing cross section in the first ion-Rydberg (n,ℓ) experiment. The first data on the projectile charge dependence of the "coincidence" cross section for electron transfer together with a vacancy in the target K-shell have been compared to coupled-channels calculations for p, α, and Li^{+3} on Ne; the good agreement provides confidence in the treatment of multielectron processes, as the projectile charge rises. The coupled-channels formalism has been improved to lift the previous restriction to systems with the ratio of $Z_1/Z_2 \lesssim 1/2$. The improved "1½" center expansion has been tested on p+H with excellent results.

Physics Division, ORNL, continued

86. MERGED ELECTRON HEAVY ION BEAMS 1.0 01-03
P. D. Miller, W. B. Dress
P. F. Dittner and S. Datz

An apparatus has been assembled consisting of a pulsed electron gun, a solenoid for compressing an electron beam and an ion charge state analyzer. A multiply charged heavy ion beam is merged concentrically with the electron beam over a one meter path interaction region. Interaction such as ionization, radiative capture, and dielectronic recombination (DR) are investigated. This third effect, known as dielectronic recombination (DR), is a resonant process — that is, for capture to occur, the electron must have just enough energy to raise an already-bound electron into an excited state and then be captured into some higher n,ℓ state. Previously, no experiments have been done in which the resonant nature of this process can be seen. The first experiments are being done with oxygen, silicon, and chlorine ion in various charge states.

87. ACCELERATOR ATOMIC PHYSICS 3.5 01-03
P. D. Miller, C. D. Moak
and P. M. Griffin

The objective of this project 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. Examples of subjects which are receiving particular attention are: 1) Coincidence studies of electron capture and loss to continuum states of projectiles, and projectile autoionizing states; 2) resonant coherent excitation of one- and two-electron ions in planar channels; 3) radiative electron capture and stopping power in channels; 4) hydrogen depth profiling in a wide variety of solid samples; 5) effects of chemical environment on x-ray hypersatellite spectra; 6) multiple electron loss cross section of heavy ions in collisions with several atomic and molecular gas targets; 7) lifetime and resonant photo-detachment cross sections of He^- ions.

88. EN TANDEM OPERATION 1.5 01-03

P. D. Miller and G. F. Wells

The EN-tandem Van de Graaff is operated for atomic physics research. Terminal voltages up to 6.5 MV are routinely achieved and the widest possible variety of heavy ions are used. Ion beams are used by personnel from the Physics Division for the Accelerator Atomic Physics Task and for the Merged Electron Heavy Ion Beam Task. Frequently, this work is collaborative with members of the Chemistry, Solid State, and Health and Safety Research Divisions. There is also a strong group of users from universities and industry. An Elbek magnetic spectrograph obtained from LASL is to be installed in FY 1981 as a replacement for the Enge spectrometer. Improvement of main beam line vacuum conditions by replacement of oil diffusion pumps and O-ring sealed aluminum tubing with cryogenic pumps and copper sealed stainless steel tubing is a continuing upgrade program. Ion source developments to increase the variety of heavy ions available also continues.

Atomic Physics

Department 4210 Sandia Laboratories--Albuquerque P. O. Box 5800 Albuquerque, New Mexico 87115	Total $124,000

89. MHD ATOMIC PROCESSES A. Wayne Johnson	1.7	01-03

The goal of this project is to measure relative transition probabilities and collisional and Stark coefficients for several lines of neutral potassium. This data is for applications in analytical measurements of electron densities and temperatures in MHD channels. Also, since alkali atoms are in many ways prototypical, this study generates a better fundamental understanding of transition probabilities, collisional line width and shifts, Stark coefficients, and relaxation phenomena. Relative transition probabilities are measured for the ns-4p (n = 6-15), nd-4p (n = 5-13), and nf-3d (n = 7-14) lines of neutral potassium with an estimated error of less than 10%. The collisional and Stark coefficients for several potassium transitions are being measured with a two-photon process, one for excitation and one for probing, that allows the determination of these coefficients for excited levels that are not strongly optically coupled to the ground level.

Chemical Energy

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Total $560,000

90. ORGANOMETALLIC COMPLEXES IN HOMOGENEOUS CATALYSIS 2.8 02-01
Robert J. Angelici

The purpose of this research is to prepare and study organometallic complexes which contain highly reactive ligands which are believed to be involved in catalytic reactions, including the Fischer-Tropsch reaction. The carbene ligand which is postulated as an intermediate in several catalytic reactions can be introduced into stable iron and tungsten complexes. Depending upon the electronic nature of the complex, carbene ligands of the type $M{=}C(OCH_3)_2$, $M{=}C(SCH_3)_2$, and $M{=}C(OCH_3)(SCH_3)$ can be highly reactive toward nucleophiles such as amines, mercaptides, and phosphines to give heretofore unknown metal compounds. It is hoped that such studies will reveal information concerning the mechanism of the Fischer-Tropsch and related reactions.

91. CHEMICAL KINETICS AND REACTIVITY OF TRANSITION METAL COMPLEXES 6.1 02-01
J. H. Espenson

This program involves the study of organometallic complexes of transition metals, especially monoalkyl derivatives such as $(H_2O)_5Cr\text{-}R^{2+}$, $R\text{-}Co(dmgH)_2B$, and $R\text{-}Rh(dmgH)_2B$. The chemical efforts consist of studies of the chemical kinetics, and reaction mechanisms of selected reactions. Effort is focused on reactions in which a metal carbon bond is formed or broken, or in which transformations or rearrangements of the organic group R occur. 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, $M\text{-}CH_2OH$ and $M\text{-}C(R,R')OH$, particularly the ease of further reaction as a function of the nature of M and of external reagents.

92. NUCLEAR MAGNETIC RESONANCE (NMR) STUDIES OF SOLID COALS AND HETEROGENEOUS CATALYSIS 6.5 02-01
Bernard C. Gerstein

Solid state techniques in NMR are used to infer chemical structures in coals, and to characterize surfaces and surface adsorbed molecules involved in hydrogen transfer reactions. Work on coals includes inferring average sizes of polynuclear aromatic rings via high resolution ^1H and ^{13}C NMR of solid coals. Evaluation of our results and conclusions is done in part via F.T.I.R. spectra obtained on coals shared with other laboratories. Of particular interest are determinations of diffusion constants of molecules such as NH_3, tetralin, and decalin in selected coals. Work on surfaces includes characterization of methanation catalysts formed by selective polymerization of Pt_nRh_m cluster complexes via high resolution solid state NMR of ^{13}C in these compounds and characterization of CO chemisorbed in zeolites in which catalytically active centers such as Ag have been deposited.

93. PROPERTIES OF RARE EARTH ELECTROLYTES 0.3 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.

94. STUDY OF SOLID-GAS REACTIONS WHICH INVOLVE STRUCTURAL CHANGES IN THE SOLID 1.3 02-01

D. L. Ulrichson and A. H. Pulsifer

Reactions such as the sulfation of calcium oxide (used for flue gas cleaning) are being studied to determine the effect of solid expansion on diffusion through the solid and on the rate of reaction. Computer models are used to describe observations and develop reactor design equations. Models have been developed to describe the pore closure which results from solid expansion by relating porosity to conversion. Steady state and unsteady state diffusion measurements are being made to relate porosity to effective diffusion rates. The solids are characterized by SEM, BET, mercury porosimetry and x-ray techniques. Conversion is measured by TGA methods.

Chemical Energy

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

Total $730,000

95. INORGANIC CHEMISTRY 4.2 02-01

E. H. Appelman, L. J. Basile,
J. G. Malm, L. Stein

The newly identified fluoroxysulfate ion, SO_4F^-, is being subjected to studies to elucidate its chemical behavior. Its reaction with inorganic reducing agents in aqueous solution appears to involve fluorine transfer with the formation of $SO_4^{-}\cdot$ radical ions. The reaction of SO_4F^- with aromatic organic compounds also appears to involve a free radical mechanism. The structure of the dixenon cation is being elucidated by electron spin resonance studies, and the equilibria involved in its formation from XeF_2 and gaseous xenon in antimony pentafluoride is being studied in detail. The study of reactions of hypofluorous acid with organic substrates that are of interest as models of biological processes continues. The oxidation of naphthalene by HOF produces the arene epoxide as an intermediate. Analogous compounds are produced in biological oxidations.

96. THERMOCHEMICAL GENERATION OF HYDROGEN 1.1 02-01

E. H. Appelman, F. Schreiner,
L. J. Basile

A thermochemical water-splitting cycle, designated ANL-4, has been developed that consists of the following four reactions:

$$2NH_3 + 2CO_2 + 2H_2O + 2KI \xrightarrow[\text{in solution}]{\text{ambient temp}} 2KHCO_3 \downarrow + 2NH_4I \quad ;$$

$$2KHCO_3 \xrightarrow{425\ K} K_2CO_3 + H_2O + CO_2 \quad ;$$

$$Hg + 2NH_4I \xrightarrow{700\ K} HgI_2 + 2NH_3 + H_2 \quad ;$$

$$HgI_2 + K_2CO_3 \xrightarrow{1000K} Hg + 2KI + CO_2 + \tfrac{1}{2}O_2 \quad .$$

Analysis of the process by means of a detailed flow diagram indicates an efficiency of 28%. Current work focuses on efforts to improve the efficiency of the process by modifying the low-temperature reaction and separation stages.

97. THE CHEMICAL NATURE OF COALS AND COAL PRODUCTS 2.8 02-01

R. E. Winans, R. Hayatsu

The aim of this research is to determine the chemical structures in coals of all ranks and of related materials such as the kerogen from oil shale. These structures are studied on both the total coals and purified macerals. A variety of chemical and instrumental approaches is being used, with particular dependence on mass spectrometry combined with chromatographic techniques. The predominant forms in which the heteroatoms O, N and S occur in coal are being identified. Direct evidence for thiophene and disulfide content is being obtained. Chemically combined long-chain aliphatic hydrocarbons are being identified in coal macerals and in the kerogen from oil shale. Studies on fluorination of coal as a probe of aromaticity are continuing.

Chemical Energy

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

Total \$300,000

98. FLUID CATALYSIS 4.6 02-01
H. M. Feder, J. W. Rathke and
M. J. Chen

The objective of this research is a detailed understanding of the kinetics and mechanisms whereby simple molecules, such as hydrogen and carbon monoxide, are converted by the use of soluble, complex transition-metal-bearing catalysts into specific organic products. The reaction of hydrogen and carbon monoxide in the presence of cobalt carbonyl hydride to yield methanol, methyl formate, ethylene glycol, and methane is being studied by a combination of kinetic, tracer, spectroscopic, thermochemical, and theoretical techniques. The results show that intermediates containing the formyl (-CHO) group and formaldehyde (π-H CO) lie on the principal pathway of the reaction. The conversion of methanol to ethanol with the aid of a new catalytic system which exhibits high specificity is also being studied by these techniques.

Chemical Energy

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

Total $150,000

99. THERMODYNAMIC CHARACTERIZATION OF CONDENSED-RING COMPOUNDS 2.5 02-01
W. D. Good

Synthesis, purification and measurement of thermodynamic properties continue on polynuclear aromatic hydrocarbons, hydrogenated polynuclear aromatic hydrocarbons, and similar compounds having the heteroatom, nitrogen, in their ring structures. All of these compounds are important in the processing of coal, oil shale and heavy ends of petroleum to produce liquid fuels and petrochemical feedstocks. Thermodynamic measurements will be made at Bartlesville Energy Technology Center on some or all of the following compounds: 1,2,3,4,5,6,7,8-octahydroanthracene, 9,10-dihydroanthracene, 1,2,3,4-tetrahydrophenanthrene, 4-methylphenanthrene, 1,2,3,6,7,8-hexahydropyrene, isoquinoline, acridine and 5,6-benzoquinoline. These studies are undertaken to form an experimental base for future correlations based on molecular structure. The comprehensive experimental program involves: (1) enthalpy of combustion, (2) low-temperature calorimetry (third-law entropy determinations), (3) vapor-flow heat-capacity calorimetry, (4) PVT relations including vapor pressure, and (5) Raman and infrared spectroscopy and molecular statistical mechanics.

Chemical Energy

Chemistry Department Brookhaven National Laboratory Upton, New York 11973	Total $515,000

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

This study of transition-metal organometallic chemistry and its relationships to homogeneous catalysis includes: (1) Catalytic Oxidations via the Nitro-Nitrosyl Couple. The short term goal of this study is the generalization of catalytic oxygen atom transfer reactions of metal nitro complexes to new substrates, particularly olefins. (2) Metal Carbonyl Derivatization as a New Approach to CO Reduction. This study is devoted to the examination of reactions which interconvert organometallic analogues of organic ketone derivatives, i.e., metal carbonyl, isonitrile, thiocarbonyl, dialkoxycarbene, etc. ligands. (3) Inelastic Neutron Scattering Spectroscopy. Development of chemical applications of inelastic neutron scattering to obtain detailed information concerning the bonding and motions of hydrogen atoms in such catalytically active species as cluster hydride complexes.

101. STRUCTURE AND BONDING IN METAL HYDROGEN SYSTEMS J. Hudis, T. F. Koetzle and M. L. Perlman	2.0	02-01

Photoelectron spectroscopy, neutron and x-ray diffraction methods, Mössbauer spectroscopy, and extended x-ray absorption fine structure (EXAFS) techniques are used to study the electronic interactions among atoms in metals, alloys, metal hydrides, and in other complex groupings such as cluster complexes. 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 relate structural results to thermodynamic properties of metal hydrides and to employ cluster compounds as models for the bonding of hydrogen atoms and small molecules to metals and metal surfaces.

102. MECHANISMS OF PHOTO-, ENZYME- & CHEMICALLY CATALYZED CIS-TRANS ISOMERIZATION 2.5 02-01
S. Seltzer

Cis-trans isomerization can be brought about by the application of heat or light or by catalysis. 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 vision in animals and the light-driven proton pump of Halobacteria. The proton pump can be utilized in a photogalvanic cell. Studies at BNL are concerned with the 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 1197

Total $680,000

103. HIGH TEMPERATURE CHEMISTRY — 3.3 — 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.

104. CHEMISTRY AND PHYSICS OF COAL UTILIZATION — 2.1 — 02-01
Thomas E. Gangwer

The objective of this program is the development of basic kinetic data on and fundamental reaction mechanisms for hydrogenation reactions. The program is investigating the kinetics of tetralin, 1,2-dihydronaphthalene, and 9,10-dihydroanthracene systems. These hydrogenations are being probed in both the gas and liquid phases. The hydrogenation/dehydrogenation mechanism for the neat hydroaromatics are heterogeneous. These systems are therefore being investigated at various gas/solid and liquid/solid interfaces. At 400°C, the gas phase dehydrogenation of tetralin over iron catalysts yields naphthalene via the reaction intermediate 1,2-dihydronaphthalene. The kinetic data follow a heterogeneous, first order mechanism which quantitatively describes the tetralin and naphthalene behavior and predicts the data observed for the 1,2-dihydronaphthalene. The kinetics of hydrogenation of the bibenzyl/stilbene system by tetralin are being studied. The mechanistic insights gained from this program are contributing to the understanding of reductive organic reactions.

105. METAL HYDRIDES 5.2 02-01
J. J. Reilly, et al

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. X-ray diffraction studies, exploiting the unique molar volume of hydrogen in metals, have shown that the anomaly in $\alpha FeTiH_x$ is due to preferential absorption of hydrogen in 3-dimensional surface phases produced by surface segregation effects and/or oxygen contamination. Similar studies are proceeding with $LaNi_5$, $TiCr_{1.8}$ and TaV_2. The influence of structure upon thermodynamic behavior of hydrogen in alloys is being examined using TaV_2. This compound exists in two allotropic forms, a bcc solid solution and an ordered Laves phase, each of which has very different thermodynamic properties. The structure of C15 $TiCr_{1.8}D_x$ is being studied by neutron diffraction. Initial results indicate that deuterium occupies the A_2B_2 site exclusively.

106. AN INVESTIGATION OF CARBON OXIDE REACTIONS 2.1 02-01
R. Sapienza

This research project is designed to investigate the validity of a synthesis gas reaction mechanism which assumes these reactions proceed via an oxygen coordinated, formaldehyde-like intermediate. The controlled decomposition and hydrogenation of proposed carbon-carbon coupling intermediates and the Fischer-Tropsch reactivity of formaldehyde using homogeneous organometallic and traditional heterogeneous catalysts indicate that certain mechanistic assumptions are valid. Current work on activating metal carbonyls for reduction via oxygen coordination with another transition metal also points to the importance of oxygen coordination in syngas reactions over metal surfaces. In a related study, two reaction pathways for the homogeneous water-gas shift reaction were found to be operative. The well-known base attack upon the carbony ligand as well as a new mechanistic pathway involving formate complexes, similar to that described for heterogeneous catalysts, should provide greater understanding of oxide interactions in catalyst systems and homogeneous analogues for heterogeneous reactions.

Chemical Energy

Energy and Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	Total $175,000

107. SELECTIVE HYDROGENATION OF COAL — 0.5 — 02-01
E. A. Grens and T. Vermeulen

This project comprises an investigation of methods for converting coal to liquid products at temperatures below the onset of coal pyrolysis (∿325°C). Conversion is accomplished with homogeneous catalysts, which achieve selective scission of certain bond types in the coal structure, and which have access to reaction sites in the extensive pore space of the coal. In this way hydrogen can be utilized more effectively and, at the same time, some of the materials and processing problems associated with the relatively severe pyrolysis conditions can be avoided. The approach used is the treatment of coal in mixtures of inorganic melts (e.g. $ZnCl_2$) and organic solvents. The melts wet the coal and serve as Lewis-acid catalysts; the solvents improve access to the coal interior, serve as hydrogen carriers, and remove initial reaction products. Coal conversions of up to 90% have been obtained in this manner.

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

The conversion of biomass to its component sugars and their subsequent fermentation to produce ethanol are the prime objectives of this work. The project investigates both enzymatic and acidic hydrolyses of biomass to hexose and pentose sugars. Basic information on the kinetics of these processes is to be obtained. High productivity fermentations to convert these sugars to ethanol or other chemical feedstocks are to be developed. Fundamental studies on 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 schemes.

Chemical Energy

Materials and Molecular Research Division — Total $940,000
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

109. HIGH ENERGY OXIDIZERS AND DELOCALIZED ELECTRON SOLIDS — 2.8 — 02-01

N. Bartlett

This research project is directed towards the synthesis of solids, the structural and redox properties of which may be of value in the fabrication of electrochemical cells and electrical-energy storage systems. The research is exploiting exceptionally powerful oxidizers to generate novel synthetic metals. The factors which control the electrical-conducting properties of graphite and other intercalation compounds, the oxidation potentials of such compounds and the reversibility of their redox reactions are being investigated. Salts, which are being derived from complex ions of non-rigid character, may provide for the facile ion transport essential for solid electrolytes.

110. TRANSITION METAL CATALYZED CONVERSION OF CO, NO, H_2 AND ORGANIC MOLECULES TO FUELS AND PETROCHEMICALS — 1.6 — 02-01

R. G. Bergman

The goal of this project is the understanding of the fundamental mechanisms of the primary steps by which organic materials undergo chemical change when they are attached to transition metal centers. Research is focused on the most general and important of these steps (i.e., those which involve the formation and cleavage of carbon-carbon and carbon-hydrogen bonds), and on processes which involve metal complexes containing one, two and three metal centers which may operate cooperatively in mediating the organic transformations.

111. FORMATION OF OXYACIDS OF SULFUR FROM SO_2 R. E. Connick	1.0	02-01

Because of its importance as a pollutant from the burning of coal, the basic chemistry of sulfur dioxide is being investigated. When dissolved, it forms a variety of species through reaction with the solvent, acid, bases and itself. More complex chemistry is introduced through oxidizing and reducing agents as well as by disproportionation of the S(IV) to higher and lower oxidation states. Studies are aimed at identifying species and their structures, measuring equilibrium constants and potentials, and establishing rates and mechanisms of reaction. Techniques used include Raman, NMR and UV spectroscopy.

112. CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION [1] H. Heinemann	1.5	02-01

This project is designed to bring to bear different skills and equipment on the fundamental aspects of the chemistry and morphology of coal. Areas under investigation are: coal pyrolysis and its primary products; observation of coal catalysis in and on the coal during pyrolysis and hydrogenation (using electron microscopy, Auger, LEED and EES, as well as MS); mechanisms of hydrogen donor action; mechansims of deactivation of coal hydrogenation catalysis; mass-transfer limitations, and metal-support interactions in Fischer-Tropsch synthesis.

[1] Jointly funded project with the DOE Office of Fossil Fuel Processing. The Fossil Energy contribution is 340K.

113. SYNTHETIC AND PHYSICAL CHEMISTRY 1.5 02-01

W. L. Jolly

Atomic core electron binding energies of a wide variety of transition metal compounds are 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 the interpretation of appropriate core binding energies, 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 distinquish 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.

114. METAL CLUSTER — METAL SURFACE ANALOGY 1.7 02-01

E. L. Muetterties

Physical and chemical studies, modeled on established molecular coordination chemistry, are directed to an elucidation of the stereochemical features of metal surface chemisorbed species generated from important organic and inorganic molecules like pyridine, aromatic hydrocarbons, olefins, acetylenes, carbon monoxide, and nitric oxide. Metal surfaces under study include nickel and platinum. The chemistry is studied as a function of surface crystallography and surface composition (carbon, sulfur and oxygen content). From such studies, the mechanistic constraints in chemisorption that lead to selective catalytic reactions are sought, e.g., in the selective hydrogenation of acetylenes to cis-olefins from the interaction of a metal surface with a mixture of hydrogen, an acetylene, and an olefin.

115. 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.

116. CONVERSION OF COAL TO CLEAN LIQUID AND GASEOUS FUELS 3.5 02-01
G. A. Somorjai, 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, and 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.

117. ORGANIC CHEMISTRY OF COAL CONVERSION 1.3 02-01
K. P. C. Vollhardt

The proposed work constitutes a program aimed at discovering novel synthetic methodology designed to achieve the transition metal catalyzed substitution of nitrogen and sulfur moieties in coal and coal-derived liquids by alternative structural units (carbon monoxide, ethylene, methylene, oxygen). For this purpose, the chemistry of transition metal complexes to hetero, mono, and polycyclic systems is being studied. Another objective includes a study of the catalytic potential of polymer supported transition metal catalysts as well as homogeneous carbyne clusters capable of methanation and Fischer-Tropsch synthesis.

Chemical Energy

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

Total $150,000

118. EFFECTS OF METAL SURFACES ON KINETICS OF HYDRIDE FORMATION 2.0 02-01
R. M. Alire and S. A. Steward

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, $LaNi_5$, 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 $205,000

119. THERMOCHEMICAL PRODUCTION OF HYDROGEN FROM WATER — 2.4 — 02-01
O. Krikorian

Thermochemical cycles for hydrogen production from water are under study with objectives to (1) find new cycles that are viable form both scientific and economic standpoints, (2) improve known cycles by innovative chemical approaches, and (3) advance the knowledge on mechanisms of reactions associated with thermochemical cycles. Work on a cycle based on ZnSe is now nearly completed, but studies on one of the reactions, the thermal decomposition of $ZnSO_4$, is continuing because it has application to several H_2SO_4 based cycles. The thermodynamic properties of $ZnSO_4$ and $ZnO \cdot 2ZnSO_4$ have been measured, and the mechanism of $ZnSO_4$ decomposition under rapid heatup conditions is under study. A study is also underway to evaluate the electrolysis behavior of water dissolved in fused salts at ∿650K. The approach is to use a mixed HBO_2/borate electrolyte, and to form LiH at the cathode by diffusing atomic hydrogen through a metallic membrane and allowing it to react with liquid Li. LiH is then thermally decomposed at ∿1200K. Paper studies are also underway to search for new higher temperature cycles.

Chemical Energy

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

Total $360,000

120. SYNTHESIS OF THERMOCHEMICAL CYCLES 4.1 02-01
M. G. Bowman, C. Hollabaugh
C. Mason and E. I. Onstott

The goals of this research project are the identification, initial evaluation and preliminary development of thermochemical cycles for the production of hydrogen from water. An important activity is the definition of criteria for the selection of cycles adapted to the characteristics of different heat sources such as nuclear fission reactors, fusion reactors and solar concentrators. Potential cycles are identified from thermochemical considerations and then tested by determinations of reaction rates, reaction yields and accurate thermochemical properties. Current studies concern: 1) mixed metal iodate-metal iodide cycles; 2) mixed metal sulfate-metal iodide cycles; 3) hybrid thermochemical-electrochemical cycles based on metal sulfate decomposition reactions; 4) hybrid cycles based on solid oxides; 5) cycles based on cadmium carbonate; 6) methods for reducing voltages required for electrochemical reactions; 7) potential hybrid thermochemical-photochemical cycles.

Chemical Energy

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

Total $190,000

121. LABILE SO_2 COMPLEXES 2.0 02-01
G. J. Kubas

The basic knowledge of sulfur dioxide chemistry is being expanded with the goal of developing new methods for scavenging SO_2 from flue gases. A two-fold approach is being taken: (1) synthesis and characterization of new transition metal SO_2 complexes which may potentially be useful in direct regenerative scavenging schemes, and (2) studies of the reactivity of SO_2 coordinated to metal complexes in order to promote catalytic reactions of SO_2 with other abundant small molecules. A successful process could convert both SO_2 and NO_x into less harmful or useful by-products. Recent results include the observation that SO_2 and NO_x are converted to sulfur, nitrogen, and water at stack gas temperatures by hydrogen reduction on a ruthenium/alumina catalyst. Methods of catalyzing such reactions homogeneously will be investigated along with further studies of the structure and bonding of transition metal SO_2 complexes. "Side-on" bonding of SO_2 is very much of interest since the sulfur-oxygen bonds have been weakened and thereby activated towards further possible reactions.

Chemical Energy

Mound Facility
P. O. Box 32
Miamisburg, Ohio 45342

Total $225,000

122. FUNDAMENTAL INVESTIGATIONS OF METAL HYDRIDES 2.7 02-01
G. C. Abell, R. C. Bowman, Jr. and
M. P. Guse

Studies are being pursued to identify and evaluate atomistic properties which influence the behavior of hydrogen in metals and lead to the formation of metal hydrides of technological interest for energy storage applications. Experimental techniques, such as NMR, XRD, and thermal analysis, are used to determine: 1) the roles of crystal structure, composition and phase transformation on hydrogen transport and storage; 2) changes in electronic structure with hydride formation; 3) effects of metal alloy substitution on hydride properties. Current experimental studies emphasize the hydrides formed from titanium intermetallic alloys, AB_5 compounds, magnesium alloys and vanadium. Quantum mechanical calculations of the electronic properties of clusters of metal atoms with hydrogen atoms are being performed based upon first principles calculations and band theory. In addition, a canonical model is being developed which describes the formation of a Jahn-Teller molecular resonance state bound to the hydrogen site in the Group Vb metal hydrides and explains most of the unusual properties of these hydrides.

Chemical Energy

Chemistry Division Total $2,040,000
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

123. INORGANIC CHEMISTRY OF HYDROGEN CYCLES 2.0 02-01
C. E. Bamberger and P. R. Robinson

New chemical reactions and inorganic compounds are studied for the development of thermochemical cycles capable of splitting water and/or CO_2. Such cycles effect the conversion of nuclear or solar energy into chemical energy in the form of burnable hydrogen and carbon monoxide, both of which also have intrinsic value as chemicals. The studies comprise the experimental assessment of chemical and thermodynamic properties of compounds, and the kinetics of the reactions involved. The results have been systematized into a model that predicts reactions which may be conducive to new cycles. This was instrumental in the identification and experimental demonstration on a laboratory scale of several new cycles. Additionally, a new family of quaternary cerium-sodium-titanates has been identified, and the chemistry and structure of these compounds have been elucidated.

124. AQUEOUS CHEMISTRY AND THERMODYNAMICS TO ELEVATED TEMPERATURES AND PRESSURES 5.0 02-01
E. G. Bohlmann, R. H. Busey, H. F. Holmes, W. L. Marshall, F. H. Sweeton

Physical chemical techniques are applied to the study of thermodynamics of processes in aqueous media at high temperatures and pressures (reactor coolants, geothermal brines, chemical processing, and waste isolation). The specific approaches now being applied are: phase studies, potentiometric, isopiestic, and calorimetric measurements. For the first time, isopiestic measurements are being made on pure and mixed electrolyte systems up to 250°C. Presently chlorides and sulfates are under investigation. Also, equilibrium measurements are being made on pure hydroxides ($\alpha Al(OH)_3$) as a function of pH, temperature, and salt medium to define metal ion hydrolysis behavior in dilute solutions. A heat flow-solution flow microcalorimeter has been developed and calibrated for measurements in solution to conditions well beyond those presently attainable (500°C and 500 bars). Presently measurements are being made on enthalpies of dilution of Na_2SO_4 and NaCl. Critical reviews, correlations, and development of equations of state are an important part of the program.

125. ORGANIC CHEMISTRY AND THE CHEMISTRY OF FOSSIL FUELS 6.0 02-01

C. J. Collins, E. W. Hagaman, L. L. Brown, B. Maxwell, M. Woody, C. Wolf

There are four current objectives: 1. elucidation of coal structures; 2. search for new methods of breaking carbon-carbon bonds in coal; 3. develop the chemistry needed for obtaining meaningful molecular weights of moieties in coals and coal-derived materials; 4. study free radical processes of the types occurring in coal liquefaction. High resolution solid state ^{13}C nmr has been employed to identify important characteristic carbons in Illinois No. 6 coal. It has been demonstrated that NaK solutions in mixed ethers will cleave both sp^3-sp^3 and sp^3-sp^2 carbon-carbon bonds in coal-like structures. Molecular weight studies have begun in collaboration with the Division's Structural Chemistry Group. Preliminary weight average molecular weights ($\overline{M}_w$) are being obtained using small angle neutron scattering (SANS). Free radical reactions of certain coal-like moieties (e.g., 1,3-diphenylpropane in tetralin at 400°) have been investigated and explained.

126. COMPARATIVE INORGANIC CHEMISTRY 2.0 02-01

P. C. Ho and R. Triolo

Aqueous-organic systems, a recurrent interest, are at present the primary concern of this program, specifically aqueous salt solutions, with amphiphilic compounds (surfactants, alcohols, and related compounds) and hydrocarbons. Macro aspects are investigated by solubilization of aqueous and hydrocarbon phases. Strong hydrotropic effects of low-molecular-weight organic salts below the surfactant range have been identified; if alcohols are also present, three-liquid-phase regions, with accompanying interfacial tensions of the order of 0.01 dynes/cm, have been found, reminiscent of surfactant-containing systems used in enhanced oil recovery. With surfactants, systematic variations of phase behavior and of interfacial tensions correlate with minor variations in surfactant structure. Micellar structure investigations are preliminary, the main effort being development of methods to combine results from light scattering and from large and small angle x-ray and neutron scattering, with use of selectively deuterated compounds, to obtain information on size of aggregates and details of molecular arrangements.

127. STEAM GENERATOR CHEMISTRY W. L. Marshall and R. E. Mesmer	1.0	02-01

The purpose of this program is to conduct in-depth research on chemical problems which limit power plant efficiency and lifetime in the steam generation stage. Transport and deposition of materials, especially oxides and phosphates, are processes occurring in corrosion and in contamination of steam generators in nuclear plants. The hydrolysis of transition metal ions and the behavior of ferrites are two principal concerns of this program. Initially we have reviewed thermodynamic data on hydrolysis reactions of metal ions important in steam systems under operating conditions. Precision potentiometric techniques are being applied to the study of the hydrolysis of cobalt(II). Details on the solution chemistry of cobalt are essential for equilibrium and kinetic models and for the control of radiation fields that affect occupational exposure levels. We are also conducting basic studies on the behavior of phosphates at temperatures to 350°C. The objective is to discover conditions and compositions which prevent corrosive environments during steam generation cycles.

128. HETEROGENEOUS CATALYSIS RELATED TO ENERGY SYSTEMS S. H. Overbury, P. A. Agron, W. C. Waggener	3.0	02-01

Our objective is to investigate the nature of chemical bonding on catalytic surfaces and its relation to catalytic activity. Three complimentary 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 on metallic crystals. Emphasis will be placed on the behavior of sulfur containing organic compounds. The second, angle resolved ion scattering spectroscopy, is used to determine top surface structures and atomic composition. Studies on stepped surfaces will be emphasized. The third method explores the tangential forces on a metal foil caused by surface adsorption through observations of macro distortions. This highly original method can be used to study the adsorbent-adsorbate forces as a function of time and surface coverage.

129\. MOLTEN SALT CATALYSTS FOR CLEAN FUEL SYNTHESIS | 4.0 | 02-01

G. P. Smith, A. S. Dworkin,
A. C. Buchanan, III

This project is a basic study of molten salt catalysts and molten salt catalyzed reactions relevant to the synthesis of clean fuels from fossil sources. Its goal is the determination of the origins of catalytic activity and selectivity to improve applications of known catalysts and aid in the search for better catalysts. Hydrocracking, hydrogenation, dehydrogenation, condensation, protonation and one-electron oxidation of polycyclic aromatic compounds are catalyzed by melts that have a posttransition metal halide, such as antimony trichloride or zinc chloride, as the dominant constituent. The effects of other Lewis acids or bases and other oxidants or reductants are determined. The formation, stability and reactions of species important in catalytic mechanisms, such as carbenium ions, organic radical cations, unstable or unusual oxidation states of metals and unusual metal coordinations in catalytically active halides are studied. Direct observations of these species in the melt are made by NMR, ESR, cyclic voltammetry, and spectroelectrochemical methods. Reaction products are separated from the melt and identified.

Chemical Energy

Chemical Technology Division Total $140,000
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

130. KINETICS OF ENZYME-CATALYZED PROCESSES 1.5 02-01
E. Greenbaum and J. Woodward

The purpose of this program is to study kinetics and enzyme catalysis related to processes for fuel production. Photobiological conversion of water to hydrogen and oxygen is an efficient technique for the capture, storage, and utilization of solar energy. Fundamental problems aimed at demonstrating the scientific and technical feasibility of photobiological hydrogen production are addressed using the chloroplast-ferredoxin-hydrogenase (CFH) system. A unique experimental approach is used to study kinetic and mechanistic aspects of hydrogen and oxygen photoproduction. Areas of investigation include (1) simultaneous light-driven photoproduction of hydrogen and oxygen; (2) long-term stability of each component in the CFH system; and (3) substitution of synthetic analogs for components in the CFH system. Using a specially-constructed flow apparatus, the simultaneous photoproduction of hydrogen and oxygen from the CFH system suggest possible strategies for developing a practical system. The stabilization of cellulase for continuous production of glucose is also being studied.

Chemical Energy

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

Total $340,000

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

This task is a basic research program whose aims 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 flash hydroliquefaction of coals and to determine sites to which hydrogen is transferred using deuterium and other labelling techniques; (3) to determine the mechanisms of formation, rearrangement and fragmentation 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 using a variety of spectroscopic and analytical techniques and to examine specific free radical reactions using the technique of flash vacuum pyrolysis of specific radical precursors, as well as other supporting methods for the controlled study of high temperature processes.

132. THERMOCHEMICAL CONVERSION OF SOLID WASTES INTO LIQUID FUELS — 3.0 — 02-01
P. M. Molton, J. A. Russell
and R. K. Miller

The objective of this project is to identify the fundamental chemical reaction mechanisms involved in the direct thermochemical liquefaction of biomass. Individual pure biomass components are liquefied in aqueous alkali at up to 400°C and products analyzed as a function of reaction temperature, alkali concentration, and reaction time. Analysis is by GC/MS and HPLC, primarily. Model compound experiments are being performed to confirm mechanistic predictions and to determine individual reaction pathways. Cellulose is liquefied through small ketonic intermediates which undergo aldol condensations, through hydrogen donor transfer reactions, and by hydrogenolytic cleavage. Work with lignin is beginning. Interactive effects occurring when two or more biomass components are liquefied together will be studied to determine reactions occurring in natural biomass.

Chemical Energy

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

Total $160,000

133. FUNCTIONAL GROUPS OF COAL AND MODEL COMPOUNDS 1.2 02-01
J. R. Morrey and G. L. Tingey

The purpose of this research is to learn how to predict the chemical reactivities of coals from a knowledge of the kinds and quantities of their structural features. Our approach is to determine the bonds most susceptible to breakage during pyrolysis, hydrogenation, and solvent dissolution, then to measure kinetic parameters which ultimately will be combined in a predictive algorithm. Current emphasis is on the interconnecting C-C and C-O-C single bonds, although S-C and N-C bonds will also be subjects of later emphasis.

Chemical Energy

Chemical and Instrumental Analysis Division Pittsburgh Energy Technology Center 4800 Forbes Avenue Pittsburgh, Pennsylvania 15213	Total $75,000

134. VIBRATIONAL SPECTROSCOPIC STUDIES OF COAL CONVERSION CATALYSTS Fred R. Brown and Leo E. Makovsky	1.0	02-01

The fundamental goal of this project is to delineate the structure of the cobalt promoted molybdenum supported on alumina catalyst system. Studies have focused on two sets of samples. In one set the cobalt concentration was held constant and the molybdenum concentration varied, while in the second set the molybdenum concentration was held constant and the cobalt concentration varied. A multi-technique approach to the problem is being taken. Raman spectroscopy is the primary technique used. These results are supported by ion scattering spectrometry (ISS), electron spectroscopy for chemical analyses (ESCA), atomic absorption (AA), and x-ray diffraction (XRD) data. The ultimate objective is to correlate the results with activity measurements. Novel supports are also being investigated.

Separations

Ames Laboratory Total $160,000
Iowa State University
Ames, Iowa 50011

135. HYDROMETALLURGICAL PROCESSING 2.8 02-02
Renato G. Bautista

The recovery of metals via a hydrometallurgical route which includes dissolution (leaching), separation and concentration (ion exchange, solvent extraction, and membrane separation), reduction to metal (cementation, gaseous reduction, and electrolysis), and the development and use of detailed mathematical models of these separation processes are related activities which comprise the principal efforts in this research task. In order to efficiently recover the valuable metal components from complex multi-metal low grade ores, the complex chemistry involved in leaching these ores is being studied. Understanding the interaction of the chemical and physical aspects of processing these ores can lead to more efficient and selective conventional and/or in-situ methods in the production of important strategic metals such as uranium, cobalt, and nickel. Improvements in the efficiency of the liquid-liquid extraction of difficult to separate metals by the enhancement of the effectiveness of one reagent with a second reagent have been successfully carried out with a rare earth system.

136. SEPARATIONS CHEMISTRY 1.0 02-02
Jack E. Powell

Work in progress is related to the group segregation of 4f and 5f rare earths from high-level wastes and partitioning of the long-lived alpha-emitting actinides from the more abundant but less hazardous lanthanide nuclides. Selective precipitation, solvent-extraction and cation-exchange-elution techniques in concert with chelate formation and synergism are the main foci of the research. A unique isolation of Am and Cm from the lanthanides exploiting the irregular behavior of diaminodiethylether-N,N,N',N'-tetraacetate as a cation-exchange eluant has been demonstrated recently and a study of additional reagent analogues and possible synergants is continuing.

Separations

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

Total $780,000

137. SEPARATION SCIENCE RELATED TO FOSSIL FUEL TECHNOLOGIES 2.4 02-02
E. P. Horwitz, G. R. Dyrkacz,
G. F. Vandegrift

This program has as its objective the development of new and improved physical separations techniques and processes that are applicable to the processing and utilization of oil shale and coal. The nature of the bonding between the organic and inorganic matrices of oil shales is being studied in order to develop new methods of enriching the organic constituents (kerogen and bituman) from the inorganic mineral constituents. The importance of carboxylic acids as surface coupling agents is being assessed. The research in coal involves the separation of the maceral constituents of coal by density gradient ultracentrifugation. Macerals of high purity are being obtained for chemical and structural characterization.

138. CHEMICAL SEPARATION SCIENCE RELATED TO NUCLEAR AND HYDROMETALLURGICAL TECHNOLOGY 8.0 02-02
E. P. Horwitz, D. Kalina, L. Kaplan,
G. Mason, R. Uphaus, G. F. Vandegrift

The aims of the separation science program are the investigation of the underlying principles of several important separation processes and the application of these principles to the development of new separation processes and techniques applicable to nuclear and hydrometallurgical technologies. The following major areas of separation science are being investigated: (1) Liquid-liquid extraction [LLE], liquid-liquid chromatography [LLC], and liquid-solid membrane [LSM] processes. New extractants are synthesized and characterized from both a theoretical and practical standpoint. Emphasis is placed on the application of liquid extractants in LLE, LLC and LSM. Studies are made of the mass transfer of metal ions through membranes and the effects of external gradients [e.g., electrical and pressure] on the selectivities of the membrane system. (2) Kinetics and mechanisms of liquid-liquid extraction and interfacial mass transfers. Emphasis is placed on developing systems in which separations are based on differential rates of extraction.

Separations

Chemistry Department Brookhaven National Laboratory Upton, New York 11973	Total $145,000

139. LASER-INDUCED REACTIONS FOR ISOTOPE SEPARATION R. E. Weston	1.6	02-02

To provide information basic to laser isotope separation, several types of laser-induced reactions are being investigated. Unimolecular reactions, bimolecular reactions, and photo-dissociation processes of vibrationally excited molecules are being investigated for the selective removal of photo-excited molecules. Details of the laser energy absorption process, energy transfer from excited species and energy flow within excited molecules are also studied because they provide basic information needed to estimate the efficiency of the specific isotope separation method used.

Separations

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

Total $125,000

140. CYCLIC SEPARATIONS PROCESS RESEARCH 2.1 02-02
F. B. Hill

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. Future work will include applications such as hydrogen recovery and purification, helium extraction from natural gas, 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 evaluation studies.

Separations

Idaho National Engineering Laboratory
P. O. Box 1025
Idaho Falls, Idaho 83401

Total $50,000

141. SELECTED ELEMENTAL SEPARATION STUDIES 1.0 02-02
Lyle D. McIsaac

The primary goal of this project is the development of methods for separating selected elements or groups of elements from nuclear waste streams. The technique being utilized is solvent extraction, and various organophosphorus bidentate extractions are being investigated. Specific studies include: actinide-lanthanide removal from bulk fission products, separation of transition metals into two groups (Zr through Tc and Ru through Pd), Hg and Cd from nuclear waste streams, higher actinides (Am and Cm) from lanthanides, and individual transition metals from each other. The extractant which has shown the most promise for these separations is dihexyl N, N-diethyl carbamylmethylene phosphonate (DHDECMP). Derivatives of this compound will be prepared and evaluated. Work during the first year is directed toward development of purification procedures for DHDECMP and preparation and evaluation of its derivatives, for actinide-lanthanide separations, survey of separation methods for second-row transition metals, and literature survey and scoping studies for potential Cd and Hg extractants.

Separations

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

Total $100,000

142. FORMATION AND PROPERTIES OF COMPLEXES OF HELIUM AND HYDROGEN ISOTOPES 1.0 02-02
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, decays with a radioactive half-life of 12.3 y. ultimately producing a pair of helium-3 atoms and a concomitant pressure increase. However, at about 21 K (-252°C) the helium-3 formed in liquid tritium is retained in the liquid in an amount far exceeding the ordinary solubility, suggesting that a metastable helium-tritium molecular complex is formed. Experiments and a parallel theoretical effort are aimed at providing detailed characterization and identification of this unusual bound species. Experiments so far have shown the complex is virtually stable in liquid tritium, is definitely unstable in gaseous tritium, has little, if any, magnetic moment, and has an effective vapor pressure less than that of the tritium host liquid. Experiments in progress will determine the electrical conductivity of liquid tritium as a function of the concentration of the complex and whether the complex is destroyed by a transport current.

Separations

Mound Facility
P. O. Box 32
Miamisburg, Ohio 45342

Total $710,000

143. ISOTOPIC EXCHANGE RATES IN H-T AND D-T MIXTURES

G. T. McConville and W. L. Taylor

0.9 02-02

The purpose of this study is to obtain a more complete understanding of the behavior 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 program. A glovebox is being outfitted with an Air Products Disphex refrigerator which will maintain a mixing chamber between 20 and 300K. The isotopic exchange rate between $D_2 + T_2$ and $H_2 + T_2$ will be measured as a function of temperature in this chamber. A special capillary sampling system leading to two specially modified mass spectrometers has been developed. One mass spectrometer measures low mass ratios rapidly with high sensitivity while the second high-resolution instrument separates HT from D_2.

144. ISOTOPE SEPARATION RESEARCH AND DEVELOPMENT

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

3.3 02-02

The purpose of this program is to investigate stable isotope separation by the methods of chemical exchange and liquid phase thermal diffusion. The primary objective of the chemical exchange work is to find significant equilibrium isotope effects in metal isotope exchange with macrocyclic polyethers. A second objective is to develop two-phase isotopic exchange systems for use in countercurrent exchange processes. The liquid thermal diffusion part of the program is directed in part toward developing improved basic understanding of the behavior of the thermal diffusion column and in part toward developing experimental knowledge about the isotopic thermal diffusion effect in the liquid phase.

Mound Facility, continued

145. INVESTIGATION OF THE MECHANISMS OF THE REMOVAL OF RADIOACTIVE NUCLIDES FROM WASTE STREAMS   0.4   02-02
G. L. Silver

The goal of this project is to investigate new methods to remove radionuclides from aqueous waste streams. An innovative technique employing both chemical adsorption combined with redox precipitation using a calcium sulfite system is being studied. Calcium sulfite is a powerful oxidizing agent which has been demonstrated to be capable of oxidizing divalent nickel to nickelic oxide, which is insoluble in water and can be removed from solution nearly quantitatively. Properties of calcium sulfite slurries are being investigated now. These property studies center upon influences on EMF of calcium sulfite slurries and testing of the slurry ability to remove cobalt from aqueous solution.

146. MOLECULAR SCIENCE RESEARCH   3.2   02-02
W. L. Taylor, R. W. York
and G. T. McConville

The objective of this project is to investigate the physical properties of stable isotopes and their mixtures. Currently, experiments are being conducted to measure total elastic scattering cross sections of the noble gases with supersonic molecular beams. Two transport properties, the thermal diffusion factor and the mass diffusion coefficient, are being determined for binary gas mixtures and their isotopes. Liquid and solid properties are being investigated by vapor pressure and heat capacity measurements. The resulting data are analyzed to probe and ascertain fundamental atomic and molecular interactions; to determine self-consistent intermolecular potential functions; and to provide information for the design and operation of isotope separation systems.

Separations

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

Total $1,955,000

147. FUNDAMENTALS OF SEPARATION CHEMISTRY — 2.0 — 02-02
C. F. Baes, Jr., F. Dowell, J. H. Burns
W. D. Arnold, F. J. Hurst

The purpose of this program is to obtain basic information and develop improved methods and processes to supply strategic materials for national energy needs. Simple theoretical models are being developed to describe the effects of chain structure and flexibility of molecular constituents on the thermodynamic properties and phase transitions of the liquid crystals,micelle solutions, and other partially ordered organic solutions used in separation processes. An investigation of inclusion complexes formed by trivalent lanthanide cations with some bicyclic diazapolyethers in water shows these complexes to be of stability intermediate between such complexes formed by alkali and by alkaline-earth cations. The separation of zirconium and hafnium by high pressure chromatography appears quite promising but is limited by the formation of polymeric hydrolysis products if the acid concentration is too low or the metal concentration is too high. Studies of octylphenyl acid phosphate to recover uranium from wet-process phosphoric acid show it to be a promising extractant, but it can be poisoned by constituents in the wet-process acid and lost to the aqueous acid by an undetermined mechanism.

148. FLOW THROUGH POROUS BODIES — 2.0 — 02-02
S.-Y. Shiao and J. S. Johnson

Processes involving fluid flow through porous media which have been of interest include behavior of chromatographic columns, mixing of fluids of different density and viscosity in passage through porous solids modeling geological formations, filtration, transport through membranes, and reactions in flow through suspensions and fluidized beds. At present, emphasis is on preparation of adsorbents in forms suitable for column operation. Many substances having attractive properties with respect to selectivity or radiation and thermal stability are difficult to prepare in particles of favorable size distribution or stability for chromatography. Impregnation of porous materials having good flow characteristics can sometimes obviate this problem. A recent example is activated carbon filled with AgCl. Short columns removed by methathesis 98% or more of iodide from solutions, at flow rates up to 4 cm/min; effective capacity was over half an equivalent per liter of bed.

149. MOLTEN SALT PROCESSES FOR HIGH LEVEL RADIOACTIVE WASTE 1.0 02-02
F. J. Smith and G. M. Begun

New aspects of the basic chemistry that relates to high-temperature nonaqueous methods of nuclear waste management are being studied. 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 10^4 for palladium from ruthenium have been determined which indicate the feasibility of isolating significant quantities of nonradioactive palladium from short-cooled fuel. The ammonium chloroaluminate system, $NH_4Cl-AlCl_3$, is a very promising solvent for nuclear waste isolation schemes because it is low melting, has a low boiling point, and has a large range of Lewis and proton acidity. Laser Raman spectroscopic studies are being conducted to study the complexing of actinides, lanthanides and fission products in chloroaluminate media.

Separations

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

Total $465,000

150. ADVANCED CONCEPTS FOR METHANE PURIFICATION 0.5 02-02
R. E. Barker and T. M. Gilliam

The fundamental goal of this project is to acquire the basic information necessary for use in a methane purification technique which will consume less energy than the existing separation technology. Advanced coal gasification processes will necessitate the separation of methane from hydrogen and carbon monoxide. The existing separation process, cryogenic distillation, is expensive and consumes large amounts of energy. A proposed absorption/fractionation process using liquid carbon dioxide as the solvent will use significantly less energy and may result in lower capital costs. Vapor-liquid equilibria data for minor components, and fundamental chemical reaction rate and equilibria data for hydrogen sulfide removal from the liquid carbon dioxide solvent are needed for a more reliable process concept. An apparatus is being designed and built and will be used to obtain the requisite basic data to evaluate the process concepts.

151. CHEMICAL ENGINEERING RESEARCH-CHEMICAL SCIENCES 5.5 02-02
J. M. Begovich, S. D. Clinton
C. D. Scott and J. S. Watson

The goals of this project are to investigate new fundamental chemical engineering concepts or unit operations which relate to utilization of energy sources, recovery of important resource materials from energy production, and control of pollutants in waste streams. A pressurized annular chromatographic device is being developed to separate several chemical components continuously. It is capable of either isocratic or gradient-elution operation. Components of an ore liquor containing Cu, Ni, and Co are being separated to study scale-up of the chromatograph. In a study of aggregation in solid-liquid suspensions in coal-derived liquids the mechanism is being elucidated by which particle suspensions are stabilized. Fundamental studies of interfacial phenomena affecting characteristics of high-temperature slagging processes are providing improvements in the recycle of scrap metals. An exploratory experimental study of the effects of microwave heating on coal conversion products indicates a high conversion of coal to acetylene.

152. FUNDAMENTAL CONCEPTS FOR RESOURCE RECOVERY 4.5 02-02
R. M. Canon, F. G. Seeley
and A. D. Kelmers

The goal of this program is to understand the chemistry and elucidate the chemical engineering principles required for recovery of valuable materials from process wastes or novel low-grade ores and for amelioration of waste environmental impact aspects. Chemical and mineralogical characterization of fly ash has yielded an understanding of the chemistry of aluminum and many other metals during the steps in the three methods being investigated: direct acid leach, Calsinter, and pressure leach. This permits selection of the most favorable treatment method for fly ashes or gasification residues from different sources to maximize resource recovery and/or trace metal control. The presence of mullite in fly ash requires basic chemicals (lime sinter or caustic digestion) to yield acid-soluble aluminum compounds. Gasification residues which have not been exposed to such high temperatures as fly ash may be more easily treated by direct acid leaching techniques.

153. FUEL CYCLE CHEMISTRY 5.0 02-02
R. L. Fellows, D. J. Pruett
and L. M. Toth

Actinide and fission product chemistries are investigated with respect to optimizing separations, minimizing wastes, and discovering new separation systems. The investigation of fundamental chemical behavior to produce better methods, or improvements in existing methods of actinide and fission product separations is the dominant theme. The studies include: (1) characterization of conditions and composition and morphology of solids formed in reprocessing solutions, (2) actinide and fission product ion complexation with solvent degradation products, (3) plutonium polymer formation, (4) solvent extraction kinetics, (5) chemistry of selected fission products (ruthenium, technetium, and tellurium), and (6) photo- and associated chemistry of the actinides and fission products. Spectrophotometry, electrochemistry, chromatography and tracer analysis are used to study realistic fuel recycle systems over a wide range of experimental conditions.

154. SEPARATIONS SYSTEMS RESEARCH 6.0 02-02

W. J. McDowell

The objective of this program is to develop new and improved chemical and physical separations methods needed in energy production. The scope includes applications to hydrometallurgy, fossil fuel conversion, nuclear fuel processing, waste treatment, and special chemical analysis. The performance and the fundamental chemical basis for the performance of various extractants are being studied, both to improve these extractants and to guide the design of new extraction systems. These include bidentate coordinating extraction by carbamoylmethylphosphonates, cation synergized size-selective extraction by macrocyclic ("crown") ethers, the powerful extraction of certain metal sulfates by primary amines, interface behavior of metallurgical amine extractants, and ternary phase systems of potential extractants for ethanol. The program also continues to develop and exploit photon-electron rejecting alpha liquid scintillation (Perals) spectrometry, and to maintain, improve, and expand a computer-retrievable data base of separations information (Sepsys).

155. SEPARATIONS CHEMISTRY FOR FOSSIL FUEL UTILIZATION 1.0 02-02

W. J. McDowell

The goal of this program is to understand and suggest applications of the chemistry of separations related to fossil fuel utilization. At present, the program is concerned mainly with removing mineral particulate matter from the unfiltered oil resulting from the solvent refined coal process-1 (UFO-SRC-1).

Two types of inorganic melts are being investigated as media for scavenging mineral particulate matter from (UFO-SRC-1): neutral salt melts and alkali hydroxide melts. The latter are more effective in reducing the mineral (ash) and sulfur content of the SRC to very low levels, but hydroxide is consumed in the process. Neutral salts may be completely reusable. Both melts appear capable of producing boiler fuel well below EPA requirements for ash and sulfur. Present studies are directed toward determining the mechanisms responsible for mineral particulate removal and optimizing conditions for this to occur.

156. TRITIUM SEPARATION TECHNOLOGY 2.0 02-02

J. B. Talbot and P. W. Fisher

The goal of this program is to obtain fundamental information on tritium separation processes required by fusion and fission reactor systems. Liquid lithium is the most promising breeding material for fusion reactor blankets, and the tritium recovery process must be efficient to maintain a low tritium inventory within the blanket system. Solid yttrium sorbents can remove tritium from liquid lithium at rates sufficient to meet process requirements. A small flowing lithium loop is used to evaluate liquid and solid phase mass transfer resistances in the sorption process. Parallel studies are evaluating the thermal regeneration of yttrium sorbents. Equilibria sorption isotherms are being measured for hydrogen isotopes and helium with different molecular sieves at cryogenic temperatures. These data are important for vacuum pumping and fuel purification techniques related to fusion energy.

Separations

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

Total $45,000

157. PYROCHEMICAL SEPARATIONS 0.4 02-02
L. L. Burger and L. G. Morgan

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 due to 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 $750,000

158. ANALYTICAL SPECTROSCOPY | 5.7 | 02-03

V. Fassel, R. Kniseley
A. D'Silva and W. Haas

In this project, particular emphasis is placed on the development of the basic science, the investigative methods, and the hardware so that trace and ultratrace inorganic and organic constituents may be characterized and quantitated in a practical manner. The major effort is devoted to the systematic observation of spectroscopic phenomena and to the development of new analytical concepts that offer promise of solving the singularly difficult analytical problems that either exist now or are likely to arise in the various fields of energy generation, the conversion of coal to liquid and gaseous fuels, solid state materials research, environmental pollution, and in the biomedical-nutritional sciences. Presently, emphasis is being placed on: (a) electrical plasmas as vaporization-atomization-excitation ionization sources for analytical atomic emission and mass spectroscopy; (b) the analytical applications of highly selective energy transfer processes from metastable gaseous species to trace inorganic or organic species; and (c) photoacoustic spectroscopy of condensed matter.

159. ANALYTICAL SEPARATIONS | 2.4 | 02-03

J. S. Fritz

The primary objective of our research is to develop innovative methods of separation and chemical analysis so that a suitable analysis technology will be available to support energy projects. A unique and effective method for separating and measuring anions has been invented which uses an anion-exchange column and a conductivity detector. This method has recently been improved and used to analyze actual samples. A similar system for cations is being developed which has been successfully used to analyze a sample containing five alkali metal ions plus ammonium in less than nine minutes. Other work concerns the development of methods for determining organic pollutants in water, and in synthesizing new resins for removing poisonous or valuable metal ions from aqueous solutions. The research on organic pollutants has resulted in new procedures for concentrating and determining acidic and basic substances in water.

160. ANALYTICAL MASS SPECTROSCOPY 3.0 02-03
H. J. Svec, R. J. Conzemius
and G. A. Junk

One project concerns methods for assaying various solids for trace impurities and dopants at levels generally below the solid-solubility limit. A scanning laser-mass spectrometer probe capable of an analytical precision of 2-5% and a spatial resolution of $\leqslant$25 μm (0.001") is being developed for this purpose. One test of this unit concerns the Mo concentration gradient in a Th bar 16.7 cm long which was the subject of an electrotransport experiment. One-hundred and ten analyses performed at various positions along the bar indicate concentrations from <1 ppm to 600 ppm. These concentration vs length data make it possible to calculate valid diffusion coefficients and transport rates of Mo in Th, important in purification studies. Another test concerns the C content of Nb/Sn dendrites in a Cu matrix, part of a development here to produce superconducting wire by a new and simple process. Manual experiments with the laser probe indicate excellent prognosis for this analysis at low to sub-ppm levels in both the Nb/Sn dendrites and the Cu matrix.

161. LASERS IN ANALYTICAL CHEMISTRY 4.9 02-03
E. S. Yeung

With the projected increase in the use of coal and other fossil fuels the emission of various forms of pollutants into the environment can become a serious problem. The need for sensitive, selective, and reliable monitoring methods for these pollutants therefore also increases. Laser analytical techniques can provide some unique insights into the production and the transport of trace elements, organics, and gaseous pollutants resulting from fossil fuel utilization. These include (1) atomic fluorescence studies on the disposition of trace elements; (2) liquid chromatographic determination of organic pollutants using more selective detectors; (3) inverse Raman excitation and acoustic detection of trace gases; (4) time-synchronous Raman as a remote monitoring tool for combustion chambers; (5) studies of spectral interference in long-path infrared absorption and infrared photoacoustic measurements of gaseous pollutants with the hope of eliminating such interferences.

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

Total $325,000

162. ANALYTICAL DEVELOPMENTS IN MASS SPECTROMETRY-CHROMATOGRAPHY AND SUPPORTING SYSTEMS 2.3 02-03
R. Hayatsu, R. E. Winans

This analytical program meets the need to characterize complex mixtures resulting from partial oxidation and liquefaction of coals. The essential instruments are high-resolution and time-of-flight mass spectrometers and a microwave plasma detector in combination with gas and liquid chromatography equipment. The chemical nature of coals is being probed by selective oxidation followed by separation and identification of the compounds produced. Quantitative data is being obtained, for example, on the different sulfur compounds of coal, as well as the O- and N-containing heteroaromatic compounds and chemically combined long-chain aliphatic compounds. Carbynes have been detected in interstellar grains, and the role of carbynes in coalification and char formation is being investigated.

163. STUDY OF ATMOSPHERIC TRACE GASES BY MASS SPECTROMETRY 2.2 02-03
C. M. Stevens, F. Rust

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 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 changes in hemispheric OH radical concentrations. The isotopic composition of methane from natural sources is being determined, and the carbon kinetic isotope effect on the reaction of methane with hydroxyl has been determined in order to evaluate the contribution of these natural sources to atmospheric methane levels.

Analysis

Chemistry Department Brookhaven National Laboratory Upton, New York 11973	Total $220,000

164. APPLICATIONS OF NUCLEAR METHODS TO ANALYSIS G. Harbottle, E. V. Sayre and R. W. Stoenner	2.2	02-03

The basic thrust of this program is to extend and improve nuclear methods of elemental analysis, particularly those methods which 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, or for which the sources of environmental pollution that has affected the trace impurity pattern of the materials analyzed are a matter of concern. Improved dating techniques by thermoluminescence and carbon 14 are being investigated: thermoluminescence as an indicator of geographic origins and as a mineral resources prospecting method; and carbon-14 dating for analysis of samples as small as 10 mg.

Analysis

Department of Energy and Environment   Total $190,000
Brookhaven National Laboratory
Upton, New York 11973

165. SPECIFIC MOLECULAR PROPERTY DETECTORS FOR CHROMATOGRAPHIC ANALYSIS   0.8   02-03

J. S. Gaffney and E. T. Premuzic

This program is developing new specific-property (SP) detectors for use in chromatography. SP detectors, whose response is proportional to a particular molecular property, will simplify separation analysis by increasing detection sensitivity for molecules of interest while reducing detector response from potential interferences. SP detectors are expected to find applications in many areas of analytical chemistry ranging from process technology monitoring to trace analysis. Detection systems for monitoring optically-active hydrocarbons using standard separation techniques are under development. A non-dispersive circular dichroism (CD) detector operated in the far-ultra violet (130-300 nm) will be used to monitor optically-active compounds eluting from a chromatograph. Since many hydrocarbons will not appreciably absorb radiation > 200 nm, use of far-UV radiation will increase detection sensitivity.

166. TRACE ELEMENT ANALYSIS USING SYNCHROTRON RADIATION   0.5   02-03

Barry M. Gordon

This project endeavors to establish a program for trace element analysis by x-ray fluorescence using the dedicated synchrotron radiation source at the National Synchrotron Light Source, now under construction. The advantageous properties of synchrotron radiation make possible the development of an x-ray microprobe with greatly improved sensitivity compared to other microprobe methods at spatial resolutions as low as one micrometer. Ray tracing calculations are being performed to establish the design parameters for a monochromator system, which will also focus the x rays of the selected energy to the highest possible intensity. Consideration is also being given to the design of a translational stage for scanning the sample with the microprobe beam. The use of wavelength dispersive detection systems in addition to the standard energy dispersive system is being investigated. A study of targeting for the microprobe has been undertaken, e.g., the deposition of individual leukocytes on a thin carbon foil backing.

167. DETERMINING FRAGILE MOLECULES IN THE ENVIRONMENT 2.1 02-03

R. L. Tanner

The long-term goals of this program are to devise and develop fundamentally-new analytical methods of high sensitivity and selectivity for the determination of traces of potentially reactive substances in the environment, based on derivatization-chromatographic separation-selective detection techniques. Derivatization is used to convert the reactive or otherwise fragile substance to a derivative which can be separated from interferences and delivered quantitatively to a detector. Chromatographic techniques (gas, liquid, ion exchange) increase analytical specificity by separating co-derivatized substances and other interferents from the derivative of interest. Selective detectors respond preferentially to specific elements or functional groups and thus greatly increase sensitivity and reduce the detector response for interferences. The derivatization-chromatography selective-detection principle is being applied to analysis of several environmental species of dynamically varying concentrations, e.g., nitrate, nitric acid, acidic sulfur compounds, ammonia, organic acids, phenols.

Analysis

Physics Department
Brookhaven National Laboratory
Upton, New York 11973

Total $150,000

168. DEVELOPMENT AND APPLICATIONS OF NUCLEAR PARTICLE MICROSCOPY

K. W. Jones and H. Kraner

2.3 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. Particle beams from a 3.5 MV Van de Graaff, MP Tandem Van de Graaff Facility and high flux reactor are used to identify isotopes through production of unique atomic and nuclear signatures and include the use of proton induced x-ray fluorescence, Rutherford backscattering, and nuclear reactions. Spatial localization is achieved by use of particle microbeams and position-sensitive detectors. For example, femtogram quantities of deuterium can be determined with a spatial resolution of 20 μm by use of the $D(t,\alpha)n$ reaction and a plastic track detector. Typical collaborative work in progress includes studies of the genetic effects arising from exposure to tritium at low concentrations, amounts of trace and minor elements contained in coal and fly ash, diffusion of heavy metals in graphite at high temperatures, and the study of trace elements in scoliosis.

Analysis

Idaho National Engineering Laboratory
P. O. Box 1625
Idaho Falls, Idaho 83401

Total $50,000

169. NEGATIVE THERMAL IONIZATION MASS SPECTROMETRY — 1.0 — 02-03
J. E. Delmore

The fundamental goals of this program are: 1) to gain a better understanding of the negative thermal (surface) ionization process, 2) to apply this knowledge to develop more efficient surfaces for converting electronegative atoms and molecules to negative ions, 3) to study the ionization efficiency of various electronegative atoms/molecules on appropriate surfaces, 4) to apply this knowledge to the development of analytical procedures for the isotopic analysis of a number of elements which can be efficiently converted to negative ions. The surfaces studied are those that have been identified as having low work functions. The elements being ionized are those that are electronegative (Cl, Br, I, S, Se, Te, etc.). Selected metal fluorides are also under evaluation. Analytical procedures are being developed for selected elements which can be efficiently converted to negative ions, with methods developed for Cl, Br and I in FY80.

Analysis

Energy and Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	Total $100,000

170. CHEMICAL ANALYSIS R. Giauque and R. Clem	1.5	02-03

The basis of this program is the development and application of trace element chemical analysis methods to support energy related research projects. The principle techniques applied are x-ray fluorescence and anodic stripping voltammetry. These techniques are used to support (1) oil shale, (2) ocean thermal energy conversion, (3) atmospheric aerosol, (4) geochemical, and (5) waste management research programs. Most of these studies are involved with studying the distribution, speciation, and fate of trace elements of possible environmental significance.

Analysis

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

Total $50,000

171. ANALYSIS OF TRANSPLUTONIUM ELEMENTS IN DILUTE SOLUTION 0.5 02-03
S. D. Brown

This project is aimed at the development of new electrochemical techniques for analysis of uranium and transplutonium elements in dilute solution. Methods under study include computer-controlled electroanalytical techniques such as staircase voltammetry and square-wave polarography. These are especially suited to the elements, U, Pu, Np, and Am, all of whom have at least one electroactive form in aqueous solution. Studies of adsorption effects will allow the direct application of these methods by providing a better understanding of the changes in electrochemical response caused by sorption of materials, thus allowing compensation for those effects. Spectroscopic methods being studied include stimulated Raman spectroscopy and photoaccoustic spectroscopy. The element Am is well suited to detection by these techniques. Construction of a general-purpose spectrometer is underway; this instrument will be used to study trace analysis of Am in water and in suitable organic extractants by liquid chromatography.

Analysis

Analytical Chemistry Division Oak Ridge National Laboratory P. O. Box X Oak Ridge, Tennessee 37830	Total $1,020,000	
172. ION MICROPROBE MASS ANALYSIS R & D: SURFACE CHARACTERIZATION W. H. Christie, R. J. Warmack and R. E. Eby	1.6	02-03

Secondary ion mass spectrometry (SIMS) provides a unique analytical capability in the areas of surface analysis, diffusion studies, depth profiling, and isotopic elemental analysis. The extreme sensitivity of SIMS makes it desirable to investigate and develop techniques for obtaining quantitative analytical information. 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. During this period, an ion optical study of a prototype cesium ion source will be conducted in an effort to improve its deliverable current density. This source will enhance our sensitivity for sputtered electronegative species and will be invaluable for studying carbide formation in nickel super alloys, a problem that leads to premature failure of reactors used in the coal gasification-liquefaction program. Cesium sputtering will allow the study of n-type dopants in silicon solar devices as an aid in improving their solar-to-electrical conversion efficiency.

173. ADVANCED SPECTROSCOPIC METHODS FOR CHEMICAL ANALYSIS L. D. Hulett, J. M. Dale and H. W. Dunn	2.4	02-03

The goal of this work is to develop and apply spectroscopic methods that are not in routine use. New techniques under evaluation and development are surface analysis by positron scattering, micro XPS in a scanning electron microscope, x-ray fluorescence and Auger spectroscopy using the Holifield Heavy Ion Facility, electron and x-ray spectroscopy with the National Synchrotron light source. Electron microscopy, x-ray photoelectron spectroscopy, x-ray fluorescence, and x-ray diffraction are being used to study electrochemical processes, high current cathodes, Zr-Hf separations, chemical species in fly ash, and corrosion processes associated with coal liquefaction. A special XPS system is being devised to study solubility problems of mixed oxides of plutonium and uranium.

174. MASS SPECTROMETRY R & D ORGANIC ANALYSES 2.7 02-03

W. T. Rainey, D. H. Russell
E. H. McBay and C. A. Pritchard

This project consists essentially of studies of fundamental ionization processes, the chemistry of gas phase ions in mass spectrometers, and various mass spectral separation techniques, leading ultimately to improved organic mass spectrometric analyses. It includes developmental studies of soft ionization techniques, such as chemical and field ionization, and application of these in methods yielding spectral and molecular structural information through various induced dissociation reactions. Various modes of scanning two and three sector instruments to yield kinetic and structural information will be studied and applied to practical analytical problems in structural elucidation. Application of these techniques to mass spectral methods for simplification of mixture analysis will result in developments utilizing soft ionization and electrical scanning modes as well as improved high resolution chromatographic and mass spectrometric techniques.

175. RESEARCH DEVELOPMENT AND DEMONSTRATION OF ADVANCED CHEMICAL MEASUREMENT TECHNIQUES 3.4 02-03

H. H. Ross, J. M. Ramsey, R. W. Shaw
W. B. Whitten, J. P. Young, L. N. Klatt

The objective of this task is to develop advanced chemical measurement systems. Work is in four broad areas: analytical applications of fiber-optic waveguides, high-resolution photoacoustic spectrometry, time-resolved fluorimetry, and micro-spectrophotometric studies of transuranium compounds. A high-speed multi-wavelength absorption spectrometer is being built by combining a laser "white light" source with the fiber-optic time-of-flight spectrometer. Fiber bundles are also being used to develop time-multiplexed detection. A piezoelectric detector will be used for photoacoustic studies of organic compounds to obtain high-resolution spectra of non-fluorescent materials. A new method for the determination of fluorescent lifetimes is being studied using an advanced laser system. This system will be applied initially to liquid chromatography effluents. In continuing studies of transuranium element chemistry, new halide compounds of Bk and Es are being examined by use of absorption spectroscopy.

176. MASS SPECTROMETRIC R & D INORGANIC AND ACTINIDES ANALYSES 2.2 02-03
R. L. Walker, D. H. Smith, R. J. Warmack
H. S. McKown, T. R. Mueller and D. L. Donohue

Inorganic mass spectrometry, thermal emission (TEMS) and spark source (SSMS), provides vital information for controlling and monitoring various programs in energy, environment, and safeguards. These MS techniques offer great sensitivity for measuring very small samples for isotopic composition (TEMS) as well as for multielement analysis (SSMS) at trace levels in essentially any matrix. Therefore, the basic objective of this task is to improve instrumentation and methodology and to develop analytical techniques which achieve highest quality measurements. Improvement of analytical accuracy and precision will be pursued by exploring methods of enhancing resin bead (TEMS) analysis of U and Pu. Computerization and software upgrading will continue. SSMS techniques will be improved through use of a beam chopper and automatic gap controller.

Analysis

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

Total $610,000

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

The objective of this program is to develop ultrasensitive analytical techniques whose basis is laser-induced atomic and molecular spectroscopy. Schemes under current investigation are based on fluorescence, photon burst and intracavity excited state absorption measurement techniques. Isotopically specific, single-mode cw dye laser excitation of radioactive iodine (I-129) is used with fluorescence detection to determine extremely low levels of I-129. In the photon burst method, a single atom passing through a laser beam can resonantly scatter many photons. Measurement of such time-correlated photons is being investigated as a method for isotopically specific single atom detection. Cesium (with its available isotopes) is being evaluated as a candidate for initial measurements. Design 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 and D. M. Robertson

The purpose of this work is to expand the utility of surface ionization mass spectrometry by increasing the sensitivity and selectivity of present techniques and by extending the method to new areas of analysis. The program has two major objectives. The first is to develop an understanding of the fundamental processes which occur during surface ionization and the effects that sample impurities and filament processing procedures have upon these processes. The second seeks to develop instrumentation for more versatile applications of and more sensitive measurements by 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, kinetics of ion production and the microchemical processes controlling composition of a sample to be loaded onto a filament. Instrumentation development utilizes a mass spectrograph which has been assembled specifically for research on both sources and detectors for mass spectrometry.

179. ULTRASENSITIVE RADIOACTIVITY SPECTROMETRIC ANALYTICAL TECHNIQUES

0.8 02-03

J. H. Kaye and F. P. Brauer

The objective of this program is to develop new and improved ultrasensitive and selective radioactivity spectrometric techniques for analysis of radionuclides. 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. Performance of 6-inch diameter by 5-inch thick phoswich detectors of the CaF_2(Eu)-NaI(Tl) type is being evaluated both as large surface area beta detectors and as beta-gamma coincidence detectors. Also, a phoswich detector composed of an organic scintillator coupled with NaI(Tl) has been fabricated and is being evaluated. Lower detection limits and greater selectivity are being sought with these detectors.

180. COMBINED ATOMIC ABSORPTION-MASS SPECTROMETRIC ANALYTICAL TECHNIQUES

1.0 02-03

D. L. Styris and J. H. Kaye

The purpose of this program is to determine the mechanisms responsible for interactions which, 1) occur at high temperatures between analyte, matrix, controlled atmospheres and furnace surfaces, and 2) 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 analyte/furnace systems being studied currently are Rb/Ta, As/Ta, Ag/graphite.

Analysis

Department 4210 Sandia Laboratories-Albuquerque P. O. Box 5800 Albuquerque, New Mexico 87115	Total $25,000

181. MASS SPECTROMETRY/LASER IONIZATION A. Wayne Johnson	0.2	02-03

The purpose of this research project is to develop the methodology for increasing the sensitivity and selectivity of mass spectrometers. Multiphoton ionization with a tunable dye laser effects this increase. The tunable dye laser selects an intermediate resonance unique to a given molecule to enhance the ionization. With the laser serving as the source of ionization in a mass spectrometer, molecules are partially preselected before they enter the mass-selection region. Particular emphasis is being given to the separation of isomers, which is virtually impossible today with mass spectrometers. The relative advantages of different mass-spectrometers (eg, quadrupole, time of flight) are being examined.

Chemical Engineering Science

Department of Nuclear Energy Brookhaven National Laboratory Upton, New York 11973	Total $50,000

182. TWO PHASE FLOW STUDIES Nesim Abuaf and Narinder Tutu	0.5	02-04

This project has two major goals: (a) the development of a simple, low cost, and objective method for flow pattern recognition in two phase gas-liquid flows, and (b) the measurement of turbulent characteristics in both phases to study the connection between turbulence and phase distributions. Statistical analysis of pressure differentials is being used to develop the flow pattern recognition techniques. An air-water loop to generate various flow regimes has been built and is being tested. It has been demonstrated that extreme care is necessary in interpreting the signals while using the piezoelectric pressure transducers in flowing liquids. Laser doppler velocimetry is being considered for turbulence measurements. To prevent the distortion of laser beams in the two phase mixture special micro-optic and fiber optic probes are being investigated.

Chemical Engineering Sciences

Energy and Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	Total $200,000

183. TURBULENT COMBUSTION F. Robben and R. Cheng	2.0	02-04

A classical turbulent flow configuration, the turbulent boundary layer over a channel wall, has been modified by heating the wall so that combustion occurs within the turbulent boundary layer. Laser Rayleigh scattering and laser Doppler velocimeter techniques are used to provide spacially and temporally resolved measurements of density and velocity. Statistical analysis of initial small scale studies has shown some interesting properties; in particular the level of velocity turbulence in the boundary layer was markedly reduced when there was combustion heat release. Extensive measurements of higher Reynolds numbers in comparison with numerical modeling are underway. The longer range contribution of this research is coupled to the development of combustion systems with low pollutant formation, high efficiency and high combustion intensity which will be able to burn new, "alternate fuels." The turbulence-combustion interaction is strongly coupled to these effects, and one path to engineering design is through further understanding of turbulent combustion phenomena and the development of satisfactory numerical computational models of turbulent combustion.

Chemical Engineering Sciences

Materials and Molecular Research Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	Total $70,000

184. HIGH-PRESSURE PHASE EQUILIBRIA IN HYDROCARBON-WATER (BRINE) SYSTEMS J. M. Prausnitz	0.4	02-04

The goal of this research is to establish a molecular framework for calculating vapor-liquid and liquid-liquid equilibria in mixtures of water and hydrocarbons at advanced temperatures and pressures. Experimental studies are in progress for the system water-methane to about 2 kilobars. Apparatus is under construction for measuring mutual solubilities in water-heavy hydrocarbon systems in the region 100-250°C. To correlate the data, a generalized Van der Waals partition function is under development.

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 0.5 02-04
P. W. Fisher

The goal of this project is to understand the fundamental physical processes which control the performance of deep sorbent beds for pumping, storing, and purifying gases. Each of three deep-bed sorption processes is studied experimentally to determine the relative importance of heat transfer, mass transfer, pressure drop, equilibrium, and reaction kinetics. Applicable physical properties are either derived from the literature or determined in separate experiments. The fundamental data are used in mathematical models to predict the performance of large deep-bed sorbent systems. These studies, once limited to laboratory-scale operations, are being utilized and proposed for large energy production and storage operations elsewhere. Future sorption pumping applications include fusion power reactors with volumes on the order of 10^5 liters, and similar scale-ups are proposed for hydrogen storage and purification 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 PROCESSES   1.1   02-04
Charles T. Li

The purpose of this project is to develop mathematical models which will 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 functions of system size and configuration, chemical reactions, and physical changes occurring with various coal conversion reactor systems. Principal tasks to be carried out during Fiscal 1980 are: (1) confirmation and refinement of gas jet and bubble coalescence models by comparison with published data and simple experimentation, (2) synthesize models to characterize heat and mass transfer phenomena occuring in fluidized and entrained suspension systems, and (3) synthesize a two-zone, three-phase model by integration of the gas jet, bubble coalescence, and transport phenomena models.

Photochemical and Radiation Sciences

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
Blacksburg, Virginia 24061

187.	REACTIONS OF CHARGED AND NEUTRAL RECOIL PARTICLES FOLLOWING NUCLEAR TRANSFORMATIONS Hans J. Ache Department of Chemistry	$80,000	01-01

The fundamental goals of this project are to understand the chemical kinetics occuring in those chemical reactions which proceed above the threshold of activation energy. Translationally excited species (atoms or ions) are generated in nuclear reactions and these interactions with various substrates are studied in order to assess the reaction efficiencies as a function of the kinetic energies associated with the reactants. Specifically, this study includes the reactions of energetic halogen species with organic compounds in solutions, the identification of the intermediates and the effect of the solvent on the mechanism, efficiency and the sterochemical course of the halogen-for-halogen exchange. An extension of this work is the application of nuclear probes such as the positron annihilation process to structural studies of micelles, microemulsions, surfactant vesicles, species which are considered essential components in solar energy conversion.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

188.	A STUDY OF INJECTED ELECTRONS IN NON POLAR CLASSICAL LIQUIDS A) HALL MOBILITY B) F.I.R. OPTICAL ABSORPTION G. Ascarelli Department of Physics	$55,000	01-01

The fundamental goal of this project is to measure the microscopic properties of the transport of electrons in insulating classical fluids. For this purpose we will measure the Hall mobility and we will search for electronic traps that exist in simple liquids and may either be intrinsic or extrinsic. During the last year most of the equipment for the Hall mobility was set up and successful trials carried out in air and insulating CdS ($\rho > 10^{10}$ Ωcm). We designed and partially built the equipment to measure the f.i.r. spectrum of electron traps in liquid rare gases.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

189. STUDIES IN CHEMICAL REACTIVITY $61,000 01-01
R. W. Carr, Jr.
Department of Chemical Engineering
and Materials Science

The 300 nm photolysis of 1,3-dichlorotetrafluoroacetone in the presence of oxygen will be investigated. Reaction product analysis by gaschromatography, fourier-transform infrared spectrometry, mass spectrometry and ultraviolet spectrometry will be done to gain information on the mechanism of the reaction of diffuorochloromethyl radicals with oxygen. Photoelectric measurements of the rate of ClO formation in flash photolysis of 1,3-dichlorotetrafluoroacetone in the presence of oxygen will be made. Flash photolysis with time resolved mass spectrometry will be used to investigate the mechanism of ketene flash photolysis and the kinetics of $CH_2(^3B_1)$ reactions. Experiments will be done to detect highly vibrationally excited molecules (~100 kcal/mole) by photoionization. Ketene, diazomethane and diazirine will be photodissociated with photons of sufficient energy to produce $CH_2(^1B_1)$, attempts will be made to detect this species via the $CH_2(^1B_1) \rightarrow CH_2(^1A_1)$ emission spectrum. Wavelength studies will be done to determine the threshold energy for appearance of the spectrum.

BOSTON UNIVERSITY
Boston, Massachusetts 02215

190. INVESTIGATIONS OF THE TRIPLET STATES OF CHLOROPHYLLS $73,000 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 <u>in vitro</u> chlorophyll systems for structural features proposed as models for the antenna and reaction center of photosynthetic systems <u>in vivo</u> and for their general applicability as model systems for photosynthesis.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

191. SENSITIZATION AND QUENCHING IN PHOTOCHEMISTRY $47,500 01-01
Stanley J. Cristol
Department of Chemistry

The purpose of this project is an attempt to define the factors affecting quantum yields and chemical yields in sensitized (and analogous unsensitized) reactions, with particular attention being paid to the phenomenon of energy wastage in such reactions. To this end, study of photosensitization, and its obverse, photochemical quenching, are being studied in a variety of organic photochemical reactions. With substrates to which a variety of reaction channels are available, different sensitizers and quenchers are being tested to see the effect upon product ratios. Fundamental data on reaction-rate constants and excitation-transfer rate constants for excited-state isomerizations and other reactions are being measured by several complimentary techniques. Possibilities of structure-reactivity correlations are being explored.

OHIO STATE UNIVERSITY
Columbus, Ohio 43210

192. PULSE RADIOLYSIS STUDIES OF FAST REACTIONS IN MOLECULAR SYSTEMS $79,254 01-01
Leon M. Dorfman
Department of Chemistry

The kinetics of fast elementary chemical reactions produced by high energy electrons in irradiated solutions are being studied by pulse radiolysis. Currently attention is focused on two types of systems. These are irradiated solutions of organic molecules in which carbocations and carbanions are generated by charge transfer to the positive charge center in the solvent and by attachment of electrons, respectively. The reactivity of the charged solute species is being determined, as well as the properties of the positive charge center. The second type of system involves transition metal carbonyl free radicals (manganese and rhenium at present). The work on the organic ionic species is relevant not only in radiation chemistry, but more broadly in organic chemistry. The work on the metal carbonyl radicals relates to homogeneous catalysis. In addition to reactivities, optical absorption spectra of these intermediates are obtained.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

193. PHOTOCHEMICAL ACTIVATION AND REACTIVITY OF POLYNUCLEAR TRANSITION METAL COMPLEX MOLECULES $80,000 01-01
John F. Endicott and Richard L. Lintvedt
Department of Chemistry

Polynuclear transition metal complexes are of considerable interest in the study of photoredox processes, since the possibility exists that concerted multi-electronic redox processes may occur. Photoinduced multi-electronic processes are of great importance since they can significantly reduce the energy requirements of processes such as the photodecomposition of water by avoiding radical intermediates. Several new binuclear complexes that are capable of undergoing multi-electron transfer are being synthesized and characterized. These include Cu(II), Cu(II); Co(II),Co(II); Mn(II), Mn(II); Pd(II) Pd(II); Cr(III), Cr(III); and Ti(IV), Ti(IV) complexes of various ligands derived from the 1,3,5-triketones. Extensive electrochemical data are being gathered on these systems using cyclic voltammetry, polarography and coulometry. These data demonstrate that the binuclear Cu(II) complexes undergo reversible two-electron reduction at one potential and, therefore, can function as multi-electron transfer reagents. The photophysics of these compounds as well as heavy transition metal binuclear complexes are being investigated.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

194. PHOTOCHEMICAL SOLAR ENERGY CONVERSION IN SURFACTANT VESICLES $52,000 01-01
J. H. Fendler
Department of Chemistry

The long range objectives of this program are the development of simple yet functional surfactant vesicles and their utilization in photochemical solar energy conversions. Surfactant vesicles mimic the functions of the biological membrane: they organize electron donors and acceptors in their compartments, provide appropriate microenvironments and allow the selective transport of substrates. The advantage of surfactant vesicles over micelles is that they are able to concentrate appreciably more donors and acceptors. Furthermore surfactant vesicles can absorb greater amounts of light than monolayers. Surfactant vesicles containing suitable electron donors and acceptors are being characterized. Attention is focussed on charge separation, facilitated electron and energy transfers and photoionization. The approach includes steady state photochemistry and flash photolysis using a nanosecond pulse laser. The obtained initial results are encouraging. Efficient charge separation had been obtained using a surfactant analog of ruthenium bispyridyl perchlorate and methylphenothiazine as an oxidation reduction couple, intercalated in positively charged surfactant vesicles. The extent of charge separation and expulsion can be optimized by the judicious addition of electrolytes which alter the surface potential and charge densities of surfactant vesicles.

THE OHIO STATE UNIVERSITY
Columbus, Ohio 43210

195. KINETICS OF FAST REACTIONS OF EXCITED SPECIES $66,230 01-01
R. F. Firestone
Department of Chemistry

The goal of this project is to determine mechanisms for growth and decay of excited atoms and diatomic molecules in pure rare gases and in the presence of foreign quenching agents. Excited atoms are formed by high energy pulsed electron beam excitation of high-lying atomic states and subsequent rapid collisional and radiative processes. Transient excited atoms and molecules are identified by emission spectrometry and fast absorption spectrophotometry. Excimers are formed via two-body and quasi-three-body excited atom reaction with ground-state species and decay via spontaneous radiative transitions at 100-1000 torr. Quasi-three-body quenching of excited atoms by foreign agents is effected by collisional relaxation of vibrationally excited excimers. A new laser detection system will substantially improve precision and time resolution.

COLUMBIA UNIVERSITY
New York, New York 10027

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

This project is aimed at the study of chemical reactions of laser pumped molecules with particular emphasis on the role of vibrational energy transfer processes in chemical dynamics. COF_2 is being pumped by an intense CO_2 laser. Photofragmentation, ultraviolet, and infrared emission are being studied to characterize the energy redistribution processes for this molecule and their effect on chemical dynamics. SF_6 is being excited by a relatively low power, continuous wave CO_2 laser. Excitation takes place in the throat of a supersonic molecular beam nozzle expansion. Analysis of the effects of laser pumping are carried out using a mass spectrometer and a bolometer. Considerable enhancement of internal energy is achieved compared to that available from simple oven heating experiments. Studies of the chemical reactivity of vibrationally excited SF_6 molecules will be carried out in a crossed beam apparatus using this excitation technique.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF TEXAS
Austin, Texas 78712

197. SOLAR ENERGY UTILIZATION BY CARBANION PHOTOLYSIS — $99,100 — 01-01
24 mo.
FY80-81
M. A. Fox
Department of Chemistry

Two aspects of photochemical conversion of solar energy are being studied in this project: photoelectrochemistry and homogeneous electron transfer reactions in excited carbanions. Organic photoelectrochemical techniques are applied to a series of highly absorptive carbanions, radical anions, and aromatic hydrocarbons. Upon photolysis such species exchange electrodes at polycrystalline semi-conductor electrodes, producing photocurrents. Excited states are being used to construct stable photogalvanic cells. A series of modified semiconductor electrodes are being synthesized and their photoelectrochemical properties examined. A mechanistic study of the photo-induced sequence of events ultimately leading to photoejection is being conducted. Quantum processes in these anions and new routes for the formation of strained compounds by intramolecular photochemical ring closures or by intermolecular photochemical bond-forming reactions are being studied.

WASHINGTON UNIVERSITY
St. Louis, Missouri 63130

198. REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS — $65,000 — 01-01
Peter P. Gaspar
Department of Chemistry

Gas-phase chemical reactions of silicon and germanium atoms recoiling from the nuclear transformations $^{31}P(n,p)^{31}Si$, $^{30}Si(n,\gamma)^{31}Si$, $^{76}Ge(n,2n)^{75}Ge$ and $^{74}Ge(n,\gamma)^{75}Ge$ are being investigated. The primary interactions of the free atoms with simple inorganic and organic molecules produce short-lived intermediate radicals and ions whose reactions are also being studied. The intermediates in recoil reactions are being compared with chemically generated species in order to elucidate the mechanisms responsible for the formation of the products observed and to define the role of excess energy and electronic state in determining the reactions that occur and their efficiency. In the past year the identification of intermediates in recoil systems has been assisted by the study of the temperature dependence of their reactivity. A new photochemical reaction sequence has provided for the first time a chemically generated synthetic equivalent of a free silicon atom. New methods have been developed for the generation of divalent silicon and germanium compounds- silylenes and germylenes.

UNIVERSITY OF FLORIDA
Gainesville, Florida 32611

199. RADIATION CHEMISTRY OF HYDROCARBON AND ALKYL HALIDE SYSTEMS $52,500 01-01
R. J. Hanrahan
Department of Chemistry

Research is directed towards understanding chemical processes which lead to formation of net products when simple chemical systems are exposed to ionizing radiation. Methods used include chemical analysis for reaction products in the presence and absence of scavengers, added to trap reactive intermediates; effect of physical variables such as pressure, temperature, and phase; and comparison with other modes of activation such as photolysis and electron bombardment in the mass spectrometer, in order to shed light on primary processes. An investigation of the radiolysis of H_2-CO mixtures includes measurement of hydrocarbon and oxygen containing products formed both in the gas phase and on reactive surfaces. Studies of CF_3I and CH_3I pulse radiolysis, as well as photolysis and mass spectrometry of mixtures of these compounds, is expected to yield details of reaction dynamics related to chemical laser work. An investigation of the radiolysis of O_2-propane mixtures is focused on the mechanism of formation of oxygen containing products.

FLORIDA STATE UNIVERSITY
Tallahassee, Florida 32306

200. RADIATION INDUCED EFFECTS IN ORGANIC SYSTEMS $40,400 01-01
Russell H. Johnsen
Department of Chemistry

Research in this laboratory is directed toward an understanding of certain basic phenomena associated with the adsorption of high energy radiation. Of interest is both kinetic and structural information involving free radicals and molecular ions.

Projects currently underway involve reactions of large free radicals in ordered solids, the structure of molecular ions as deduced from solid target collisional activation (STCA) studies and the kinetics of reactions of hydroxyl radicals with organic molecules in the gas phase. The free radical studies involve a series of azoxy compounds of rod-like shape with specific steric requirements for radical-radical recombination. Both diffusional and torsional activation energies are being measured. Molecular ions under investigation are studied with the objective of determining if the source of the ion determines structure or if electron impact always results in the structure of lowest energy. The gas phase radical reactions are designed to simulate certain processes important in atmospheric chemistry.

BOSTON UNIVERSITY
Boston, Massachusetts 02215

201. ORGANIC PHOTOCHEMICAL STORAGE OF SOLAR ENERGY G. Jones, II Department of Chemistry	$72,000	01-01

Valence photoisomerization is investigated with emphasis on mechanisms of photosensitization involving either electron-donor-acceptor interaction or energy transfer. Formation of excited complexes of donor-acceptor isomerizable substrates and sensitizers results in efficient rearrangement for substrates including norbornadiene derivatives, quadricylene, and hexamethyldewarbenzene. Irradiation of charge transfer bands of ground state donor-acceptor complexes also leads to rearrangement reactions. Energy transfer from a sensitizer, benzanthrone, to norbornadiene-2,3-dicarboxylate is temperature dependent. Kinetics are consistent with endoergic energy transfer for this system, allowing an assessment of the benefits of thermal activation of low energy excited species.

UNIVERSITY OF ILLINOIS
Urbana, Illinois 61801

202. ELECTRON TRANSFER IN SYSTEMS WITH A WELL-DEFINED GEOMETRY K. J. Kaufmann Department of Chemistry	$55,000	01-01

Cyclophanes formed by joining two chlorophyll molecules together with two covalent linkages are being studied. The aim of this work is to understand the criteria that govern efficient light induced electron transfer. The electrochemical properties of the cofacial dimer can be altered by adding one or two magnesium atoms. The solvent environment can also be modified. The electron transfer reaction is started by exciting the cyclophanes with a short burst of light. The conversion of the light pulse to an electron and a positive hole is followed by both absorption and fluorescence spectroscopy. The experiments indicate that the electron transfer process occurs very rapidly. The major portion of the charge is neutralized in about 300 picoseconds. A small fraction appears to last about ten times longer. Presently the mechanism for stabilizing the small fraction of the charge is under study.

UNIVERSITY OF CALIFORNIA
Santa Barbara, California 93106

203. 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. Previous work has shown that solutions containing EDTA or citrate enhance photocurrents, and therefore solute effects are being studied in greater detail including other carboxylic acids. Chemical analysis of the photoproducts is being carried out using mass spectrometry, coulometric titration, gas chromatography and HPLC. n-Fe_2O_3 is produced thermally (1000-1300°C) or by chemical doping (*e.g.*, addition of TiO_2). Competition for light produced holes at the iron oxide electrode surface is observed in basic solutions containing iodide ions. Little iodine is produced when solutions are unstirred, but essentially all photocurrent leads to I_2 production in stirred, 1M KI solution.

LOUISIANA STATE UNIVERSITY
Baton Rouge, Louisiana 70803

204. THEORETICAL STUDIES OF EXCESS ELECTRONS IN FLUIDS: STRUCTURE AND ELECTRON TRANSFER — $33,400 FY79-80 — 01-01
N. R. Kestner
Department of Chemistry

The goals of this project are to better understand the traps of electrons in polar media and electron transfer reactions in fluids. Ab Initio calculations are being made on electrons trapped in clusters of water, ammonia, and alkali halide formula units. Detailed studies are also underway on the role of exothermicity, temperature, non-adiabaticity, and the failure of the Condon Approximation for electron transfer reactions. These results are now being applied to reactions of trapped electrons. Further studies on metal ammonia solutions are also indicating that clusters of two trapped electrons and a cation are reasonable spin paired species at higher metal concentrations.

Photochemical and Radiation Sciences, continued

UNIVERSITY OF HOUSTON
Houston, Texas 77004

205. 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 design more efficient systems and to eventually couple this charge separation to chemical energy storage. The monophotonic photoionization of N-heterocyclics and chlorophyll in anionic, cationic and nonionic micellar systems in the presence and absence of added electron acceptors will be studied by electron spin resonance, electron spin echo spectrometry and kinetic electron spin echo spectrometry. Conditions for maximum photoionization efficiency including the structural location of the photoproduced cations in the micelle will be sought.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

206. RADIOLYSIS STUDIES OF REACTIVE INTERMEDIATES $50,000 01-01
6 mo.
Larry Kevan
Department of Chemistry

The fundamental goals of this project are to understand the reactivity and electronic and geometrical structure of highly reactive chemical intermediates generated by radiolysis and photolysis. The detailed geometry of solvated electrons in matrices of varying polarity is being studied by newly developed applications of electron spin echo spectrometry. These methods are also being used to study the solvation of atomic intermediates and to study preferential solvation in mixed matrices. New evidence for presolvated electrons having a nonequilibrium solvation shell in polar media is being obtained by radiolytic generation at 1.6K followed by optical absorption studies at the same temperature. Pulse radiolysis and laser photolysis studies are helping to clarify the kinetics and mechanism of electron solvation in both pure and mixed matrices.

UNIVERSITY OF ALABAMA
University, Alabama 35486

207. ELDOR INVESTIGATIONS OF RADIATION PROCESSES — $49,000 — 01-01
L. D. Kispert
Department of Chemistry

The goal of this project is to determine how a crystalline lattice affects energy transfer and primary radiation processes in irradiated organic crystals. Such information is vital to understanding 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. Relaxation processes are being measured as a function of irradiation and annnealing temperature.

JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

208. STUDIES IN HOT ATOM AND RADIATION CHEMISTRY — $72,300 — 01-01
Walter S. Koski
Department of Chemistry

The objective of this study is to realize an understanding of the ionic aspects of hot atom processes associated with nuclear transformations and radiation chemical reactions. Currently our effort is being concentrated on the bromine-ethane hot atom system. Using ion beam techniques the cross sections of the various reactions of Br^+ with ethane are being measured. Since rare gas moderators are widely used in the study of hot atom reactions, the role played by the moderators in these processes is also being studied. The moderators are found to be not "inert" but they participate in an active chemical way in the hot atom reaction. Ions such as $KrBr^+$ and CH_3BrKr^+ play an important role in the bromine-ethane hot atoms system. The properties and reactivities of these ions are also being studied.

Photochemical and Radiation Sciences, continued

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

209. STUDIES IN CHEMICAL DYNAMICS Aron Kuppermann Division of Chemistry and Chemical Engineering	$129,000	01-01

The objective of these studies is the understanding of the dynamical consequences of the collisions of molecules with other particles: electrons, photons or other molecules. Triplet excited states of a large variety of molecules are being investigated by electron impact, photoacoustic and multiphoton ionization spectroscopy. The electronic states of ions are being investigated by variable angle photoelectron spectroscopy. A high energy-high intensity beam of hydrogen atoms is being used to study their chemical reactions. Crossed molecular beams are being used to study intermolecular forces. The dynamics of photochemical processes are being investigated by variable wavelength laser-induced photolysis. These investigations are useful for the elucidation of the energy flow in molecular collission processes.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

210. THE PHOTOCHEMISTRY AND RADIATION CHEMISTRY OF VOLATILE SILANES AND GERMANES F. W. Lampe Department of Chemistry	$81,212	01-01

The goals of this project are to understand the fundamental reaction mechanisns of the photochemical and radiation chemical induced decompositions of gaseous silanes, germanes and phosphines. The decompositions of phosphine and methylsilane by the absorption of vacuum-ultraviolet light are being studied by a mass-spectrometric technique in which all reaction products are monitored continuously as a function of time and it has been possible to draw fundamental mechanistic conclusions about these chemical conversions. The same technique is being applied to a study of the multiphoton infrared induced decomposition of monosilane. The lifetimes and stabilities of collision complexes formed in the reaction of silyl ions with ethylene and the dependence on internal energy of the complex are being examined using a tandem mass-spectrometric apparatus. The existence of protonated monogermane in the gas phase has been demonstrated for the first time, using the same apparatus. It has been possible to show that the proton affinity of monogermane is greater than that of monosilane.

BRANDEIS UNIVERSITY
Waltham, Massachusetts 02154

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

Interaction of excited molecules with electron donors or acceptors may lead either to energy dissipation (quenching) or radical-pair formation. The latter process is the first step in photochemical conversion of light energy. A primary goal of this research is therefore the elucidation of the factors governing the efficiency of radical formation in photo-redox reactions. The factors being studied include solvent polarity, viscosity, excited state spin multiplicity, redox potential, external fields and specific reagent structure. Electron-transfer rates are being obtained by luminescence quenching (for singlet excited states) and by laser flash photolysis (for triplets). Primary radical yields are derived from the flash data, for systems in which excited state and radical extinction coefficients are available. In cases where quenching involves spin-reversal (triplet excited states), the effects of imposed magnetic fields and deuterium substitution are being studied, in connection with possible hyperfine mechanisms for spin rephasing.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

212. THE CONTRIBUTION OF ELECTRONICALLY EXCITED STATES TO THE RADIATION CHEMISTRY OF ORGANIC SYSTEMS Sanford Lipsky Department of Chemistry	$80,000	01-01

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) Determination of the energy threshold and energy dependence of the quantum yield for photo-ejection of electrons from solute molecules in nonpolar condensed phases via measurement of the ionization current and ion + electron recombination fluorescence. b) Measurement of the fluorescence quantum yields of highly excited states of some simple aromatic and olefinic molecules in order to evaluate the rates of non-radiative decay of these states and to determine the nature of their decay channels. c) Measurement of the electron impact energy-loss spectra of some olefinic and saturated hydrocarbon molecules to assist in the characterization of their electronic states.

UNIVERSITY OF KANSAS
Lawrence, Kansas 66045

213. STEREOELECTRONIC PROPERTIES OF AGGREGATED CHLOROPHYLL SYSTEMS G. M. Maggiora Department of Chemistry	$76,400	01-01

The primary goal of this project is to develop an understanding of the geometric and electronic structural features of monomeric and aggregated chlorophyll species and their relationship to energy conversion in photosynthetic and related systems. The studies are being carried out using both quantum mechanical and empirical potential function techniques. In particular, ab initio configuration calculations are being used to investigate the energies, oscillator strengths, and polarizations of the singlet-singlet and triplet-triplet transitions of neutral chlorophylls and the doublet-doublet transitions of their corresponding π cation and anion radicals. Calculated state energy diagrams are also being used to elucidate the photophysical properties of these molecules, and calculated spin density distributions are being used to aid interpretation of hyperfine coupling constants. Quantum mechanical and empirical potential function calculations currently in progress are being used to investigate the structural chemistry of the chlorophyll special-pair dimer present in the PSI phototrap of plants.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

214. PRINCIPAL PROCESSES IN THE RADIOLYSIS OF GASES WITH FISSION RECOILS AND GAMMA RAYS G. G. Meisels Department of Chemistry	$85,000	01-01

This project has two primary goals: 1. The determination of reaction and momentum transfer rate constants, thermodynamic properties, and fragmentation mechanisms resulting after collisions of molecules with ions produced by energetic electrons and heavy ions. Mass spectrometry, with the ion source at pressures up to three torr, is used. Ions are mass analyzed by a magnetic sector and the effect of composition, electric fields and temperature on residence time distributions is measured. Also measured is the range of electrons with energies of 100 to 500 eV in a variety of gases. 2. The evaluation of unimolecular rate constants, structure, unimolecular rearrangements, and barriers towards isomerization of state selected organic ions. These studies employ threshold photoelectron-coincident photoion, high resolution, and collision induced dissociation mass spectrometry. Isomerization of C_4H_8 ions, of methylnitrite and nitromethane, and of propane ions labelled centrally with C-13 are under investigation.

UNIVERSITY OF NORTH CAROLINA
Chapel Hill, North Carolina 27514

215. ENERGY CONVERSION BASED ON MOLECULAR EXCITED STATES T. J. Meyer Department of Chemistry	$73,500	01-01

The photochemical and photophysical properties of metal complex excited states are being investigated with the goal of developing useful energy conversion schemes. Redox quenching of polypyridine complexes of Ru or Os or direct photolysis of organic donor-acceptor complexes leads to chemical changes which provide the basis for a series of different photoelectrochemical applications. Detailed photochemical (quantum yields and products) and photophysical (lifetimes and emission efficiencies) studies on spin-paired d^6 complexes are giving insight into the factors of excited state structure and reactivity which determine excited state lifetimes. One result of the study has been the preparation of a series of polypyridyl complexes of Os(II) which are highly luminescent and long-lived. Polymers containing some of the polypyridine Ru chromophores have been prepared and their excited state properties are currently under investigation.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

216. FLASH PHOTOELECTROCHEMICAL STUDIES OF TRANSIENT ELECTRODE PROCESSES IMPORTANT IN SOLAR ENERGY CONVERSION Sam P. Perone Department of Chemistry	$60,000	01-01

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

216a. INTRAMOLECULAR ENERGY TRANSFER REACTIONS AS A METHOD FOR METAL COMPLEX ASSISTED PRODUCTION OF HYDROGEN $72,896 01-01
John D. Peterson
Department of Chemistry

This research seeks to photochemically produce molecular hydrogen from a transition metal dimeric compound. The metal centers making up the dimer have different characteristics and functions in the system. A metal center containing ruthenium(II) or ion(II) and an aromatic nitrogen heterocyclic ligand will function as the light absorbing metal center. The second metal center is the reactive metal center which will contain two hydride ligands in a <u>cis</u> configuration. The design of the system, which includes the antenna fragment, reactive fragment, and bridging ligand must fulfill the following requirements: 1) The relative energies of the excited states in the antenna fragment must be tuned such that no photochemical reaction occurs at this metal center, 2) the bridging ligand must allow communication between the excited states localized mainly on the antenna and reactive fragments, and 3) the non-reactive state populated on the antenna fragment must be able to transfer energy to an excited state localized on the reactive fragment which results in the elimination of molecular hydrogen.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

217. HIGH ENERGY HALOGEN REACTIONS ACTIVATED BY NUCLEAR TRANSFORMATIONS $48,000 01-01
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 biomolecules. 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 biomolecules are being carried out.

Photochemical and Radiation Sciences, continued

CARNEGIE-MELLON UNIVERSITY
Pittsburgh, Pennsylvania 15213

218. PHOTODECOMPOSITION OF WATER IN HOMOGENEOUS SOLUTION Robert M. Richman Department of Chemistry	\$60,000 15 mo. FY80-81	01-01

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. The photodecomposition of water into hydrogen and oxygen will require efficient photo-oxidants and photo-reductants. Permanganate is a model to effect the photochemical generation of oxygen, and one study aims to determine the generality of this mechanism in related compounds. In addition, we observe compounds of the form MoO_2L_2, L = dialkyldithiocarbamate or benzacetylacetonate to do photochemistry. Electronic absorption, esr, gc, and cyclic voltammetry experiments are aimed at determining reaction products, quantum yields, and mechanisms. Companion theoretical calculations seek to verify the generality of these and other mechanisms for energy storage.

THE JOHNS HOPKINS UNIVERSITY
Baltimore, Maryland 21218

219. FAR INFRARED CHEMICAL LASERS Dean W. Robinson Department of Chemistry	\$74,000	01-01

The focus of this research is on the energy transfer processes, both inter- and intramolecular, that take place in reacting gas-phase mixtures between the time of product formation and the output of stimulated emission pulses. Population inversions are established optically, either by photochemically initiating reactions or by simple (non-coherent) photon absorption. The time behavior of the output pulse reflects the dynamics of the molecular processes involved in the sequence. The diatomic molecules OH, NH, and HF have been prepared by different methods; their different nascent vibrotational energy distributions have been monitored in time by observing the pure rotational laser action resulting from rapid V→R transfer. Submillimeter lasing in HCN has been studied as a function of the reaction producing the inversion and the collision partners relaxing it. Water has been inverted by chemical reaction, E→V transfer, and most recently, the first optical pumping using an incoherent light source. There is promise here for extension to many other polyatomic systems.

UNIVERSITY OF CALIFORNIA/DAVIS
Davis, California 95616

220. NUCLEAR METHODS IN CHEMICAL KINETICS $60,000 01-01
John W. Root
Department of Chemistry

The goals of this project include the following: (i) To develop sensitive radiotracer methods for measuring chemical reaction rates under both equilibrium and nonequilibrium conditions; (ii) To understand the bimolecular kinetic behavior of energetic monovalent atoms produced from nuclear reactions; and (iii) To understand the unimolecular kinetic behavior of excited polyatomic molecules activated via radical combination or hot atom substitution reactions. The reactions of hot ^{18}F atoms produced from the $^{19}F(n,2n)^{18}F$ nuclear reaction are being investigated with gaseous CF_4, C_2F_6, and CF_4/H_2 mixtures at effective pressures (P/Z) of 0.5-200 kTorr. Bimolecular rate coefficients are obtained for thermal ^{18}F atom reactions via the moderated nuclear recoil (MNR) technique. The gas phase $CH_4/C_3F_6/C_2F_6$ and alkane/C_2H_4/C_2F_6 ^{18}F MNR systems are presently under study at various (P/Z) values and system compositions. The unimolecular kinetic and energy transfer behavior of $^{14}CH_3CF_3$ produced via $^{14}CH_3 + CF_3$ combination is being determined at 300°K and 0.001-1 kTorr (P/Z).

UNIVERSITY OF CALIFORNIA
Irvine, California 92664

221. RESEARCH IN CHEMICAL KINETICS $150,000 01-01
F. Sherwood Rowland
Department of Chemistry

The reactions of halocarbons and other species in the atmosphere are studied using photochemical and hot atom techniques. Reaction types under study include $^{18}F/X$ substitution reactions with CH_3X molecules (X=halogens; small group substituents); the formation of $R^{18}F$ from R_4M (M=Si, Ge,Sn; R=CH_3, vinyl, allyl) and addition to Π-bonds (CH_2=CHCl, (allyl)$_4$M, alkenes, alkynes. Reactions of ^{38}Cl with CH_4, C_2H_6, c-C_3H_6, CH_2=CHBr, etc., are carried out over a range of mole fractions, and between 240-360K to investigate the transition from mixed hot+thermal systems to thermal reactions alone. The chemical pathways in the atmosphere are being evaluated for cosmogenic tritium and for cosmogenic *Cl (^{38}Cl and ^{39}Cl), including formation of H*Cl, *ClO, *$ClONO_2$, and HO*Cl. Some photochemical experiments are being carried out with CHTCO and $^{14}CH_2CO$ to investigate further the mechanistic aspects of methylene reaction with hydrocarbons and halocarbons in the gas phase.

WORCESTER POLYTECHNIC INSTITUTE
Worcester, Massachusetts 01609

222. THE GAS PHASE RADIOLYSIS AND VACUUM ULTRAVIOLET PHOTOLYSIS OF HETEROCYCLIC ORGANIC COMPOUNDS — $32,980 — 01-01
Alfred A. Scala
Department of Chemistry

We are studying the high energy radiation chemistry of heterocyclic organic compounds. This work is enhancing our understanding of the high energy chemistry of organic compounds. General principles elucidated can be used to understand and predict the high energy chemistry of the large number of compounds which cannot be studied individually. This capability is essential to our understanding of the high energy chemistry of organic compounds. Some of the generalizations we have arrived at include: (1) The excited states originally populated are relatively unimportant because the lifetimes of the excited molecules are sufficiently long to enable the establishment of a quasi-equilibrium, which permits the sampling of potential energy surfaces and the influence of thermodynamic factors upon the competition between reaction channels; (3) initial cleavage of the carbon to hetero-atom bond is most consistent with the information gathered; (3) the subsequent cleavage of the initially produced diradical depends upon the number of atoms between the diradical centers and the oxidation state of the heteroatom.

CHARLES F. KETTERING RESEARCH FOUNDATION
Yellow Springs, Ohio 45387

223. PARTICULATE MODELS OF PHOTOSYNTHESIS — $50,000 — 01-01
G. R. Seely

The primary goal is to develop model systems with chlorophyll which are concentrated in pigment and yet retain excited state reactivity comparable with that of green plant membranes. The system employed consists of particles of polyethylene, swollen with plasticizers such as undecane, to which are adsorbed chlorophyll and other amphiphilic substances. The intent is to provide the particles with a viscous surface in which the hydrophobic parts of chlorophyll and surfactants can be embedded, and thereby to preserve excited states and reduce fluorescence quenching through restriction of molecular motion, even when the chlorophyll concentration is high. In most of the systems examined, there is evidence of specific association of chlorophyll with the surfactant, and of aggregation of chlorophyll into fluorescent structures not wholly dissimilar to those present *in vivo*.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

224. DYNAMICS AND MECHANISMS OF HOT CHEMISTRY Leonard D. Spicer Department of Chemistry	$60,000	01-01

This research is designed to explore reaction kinetics, atomic and molecular collision dynamics, and energy transport at energies significantly above thermal thresholds. Intermolecular energy transfer following nuclear recoil chemical activation is being studied. Concurrent reactions of recoil ions in selected bath gases are also being investigated to identify mechanistic similarities and differences in excited neutral and carbonium ion systems. A sequential trajectory analysis is being developed to study the generality of the moderated nuclear recoil technique for measuring relative thermal rate constants. Photochemical and thermal kinetics and mechanisms of sulfur dioxide reactions with hydrocarbons and silyl hydrocarbons are also being investigated. Ultraviolet radiation in the energy range of natural sunlight at the earth's surface is used to excite the sulfur dioxide and laser induced ultraviolet fluorescence at higher energies is used to follow the reaction. Analytical techniques for product detection involving stimulated fluorescence, chromatography, and mass spectroscopy both directly on the molecules and on silyl derivatives are being developed.

MOUNT HOLYOKE COLLEGE
South Hadley, Massachusetts 01075

225. PHOTOELECTROCHEMISTRY OF ORGANIC DYES Mark T. Spitler Department of Chemistry	$39,900	01-01

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 TiO_2 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

226. HOT ATOM REACTIONS INVOLVING MULTIVALENT AND UNIVALENT $45,000 01-01

Y.-N. Tang
Department of Chemistry

The purpose of this project is to study the reactions of various types of energetic atoms. The major progress during this period is in the study of recoil silicon-*31* and carbon-*11* reactions. Heterogeneous hydrogenation experiments confirm that a major unknown product, derived from the interaction of silicon-*31* atoms with 1,3-butadiene, is 1-silacyclopenta-2,4-diene. Another set of experiments reveal that the stepwise abstraction mechanism is definitely much more predominant than the possible simultaneous abstraction by silicon-*31* atoms. On the other hand, the degradation of the carbon-*11*-labelled propadiene derived from the reactions of recoil carbon-*11* atoms with ethylene shows that 73% of the propadiene is center-labelled. This value is observed to change with additives: (i) to 100% with 40% oxygen; (ii) to 83% with 92% xenon; and (iii) to 6% with 94% neon.

UNIVERSITY OF KENTUCKY
Lexington, Kentucky 40506

227. ELECTRON PHOTOEJECTION IN CARBANIONS $45,000 01-01

Laren M. Tolbert
Department of Chemistry

The efficiency of electron photoejection by resonance-stabilized carbanions is a function of the balance between excitation energy, oxidation potential, and anion stability. The exact way in which these variables affect the efficiency is the subject of our current study, which involves dimethyl sulfoxide as an irreversible electron acceptor from photoexcited carbanions related to triarylmethane dyes. Carbanions substituted by electron releasing groups are more efficient, but the cost in terms of available excitation energy has not been determined. Conversely, anions characterized by a high degree of aromaticity are less efficient but are probably capable of ejecting electrons at higher potentials. The goal is to achieve a sufficient understanding of these and other structural parameters in order to obtain the optimum between quantum efficiency and available excited state potential.

UNIVERSITY OF ARIZONA
Tuscon, Arizona 85721

228. MECHANISMS OF PHOTOCHEMICAL ENERGY CONVERSION BY CHLOROPHYLL $55,000 01-01
Gordon Tollin
Department of Biochemistry

The excited state dynamics and the yields and lifetimes of radicals are being investigated in systems containing chlorophyll and electron acceptors dissolved in lipid bilayers or polymer films. Laser photolysis and electron spin resonance are being used in these studies. The proposed work involves the effects of variations in the lipid composition of the bilayers, especially as related to viscosity and surface charge, the use of quinone polymers as media, the effect of variations in acceptor structure and redox potential, and variations in donor properties (e.g. use of pheophytin or bacteriochlorophyll in place of or in addition to chlorophyll). Particular emphasis is being placed upon developing strategies to increase radical yields and lifetimes with a view towards the possible construction of solar energy conversion systems.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

229. PHOTOINDUCED INTERACTIONS OF TRANSITION METAL COMPLEXES WITH WATER $45,000 01-01
Richard J. Watts
Department of Chemistry

This research program is designed to probe photoinduced chemical and physical energy conversion processes in solvated transition metal complexes. Emphasis is being placed on N-heterocyclic complexes of the heavier group VII metals. Rates and mechanisms of photosolvation processes are being studied by laser flash photolysis. Conventional and laser flash techniques are being employed to study rates and mechanisms for photoinduced electron transfer processes. Interactions of excited states of Ir(III) complexes with species such as OH$^-$ and Br$^-$ are being studies to evaluate their potential for driving useful chemical oxidation processes. The nature of the transients formed in reductive quenching of excited states of Ir(III) complexes is being studies by flash photolysis of aqueous solutions of the complexes with Eu(II). Transients are being characterized by time-resolved absorption spectroscopy. Ground state reductions by conventional chemical means are being carried-out for comparison with the flash photolysis results. Solvated ground state structures are being studied by ^{1}H and ^{13}C NMR.

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

230. STUDIES IN HOT ATOM AND RADIATION CHEMISTRY $35,500 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, ions, and complexes formed in solid organic matrices at 4 K - 200 K by ionizing radiation, by photolysis, and by metal photosensitization. The species under study 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 in the work is on the mechanisms of free radical production in radiolyzed hydrocarbons, on the mechanism of abstraction of hydrogen from carbon-hydrogen bonds by hydrogen atoms at cryogenic temperatures, and on the production and reactions of trapped hydrogen atoms in CH_4, CD_4 and in rare gas matrices containing organic solutes.

UNIVERSITY OF TENNESSEE
Knoxville, Tennessee 37916

231. RESEARCH CONCERNING IONIC AND FREE RADICAL REACTIONS IN RADIATION CHEMISTRY $78,000 01-01
T. F. Williams
Department of Physics

The objectives of this project are to identify novel free-radical intermediates and to study radical reactivity, mainly by means of electron spin resonance (ESR) spectroscopy. Radicals are produced by the irradiation of solids at low temperatures, this technique being particularly useful for the generation of a wide variety of radical anions derived by electron attachment to molecules. By a suitable choice of solid matrix, the isotropic or anisotropic ESR spectrum of the trapped radical can be obtained. The electronic structures and geometries of high-energy paramagnetic species such as CF_3Cl^-, $(CF_3)_3CI^-$, and the perfluorocycloalkane radical anions are being studied by measurements of the hyperfine coupling constants, including those for ^{13}C-labeled compounds. The chemical reactivity of radicals in hydrogen-atom transfer reactions is also being investigated. Deuterium isotope effects and rate constants are being measured at cryogenic temperatures, and the results are interpreted in terms of a quantum-tunneling model which incorporates zero-point energy effects.

GENERAL ELECTRIC CORPORATE RESEARCH AND DEVELOPMENT
Schenectady, New York 12301

232. STUDY OF PHOTOCHEMICAL EFFECTS USING STABLE SEMICONDUCTOR ELECTRODES — $120,000 — 01-01
R. H. Wilson — 24 mo.
Energy Sciences Branch — FY79-80

Studies are underway in which a new technique for investigating layers of organometallic compounds is being evaluated. The material to be investigated is deposited on the surface of stable semiconductor electrodes of known behavior. The semiconductor is excited by light of sufficient energy to produce bandgap transitions and this energy is transferred via minority carriers to the surface coating. Electron transfer to and from these layers is being investigated in the context of a previously developed model for charge transfer at semiconductor-electrolyte interfaces. Chemical and physical properties of the layers are being inferred from these investigations. Using this technique, previously investigated materials such as rhodamine-B and ruthenium tris-bipyridyl are being studied. In addition, new compounds have been synthesized and attached to TiO_2 and $SrTiO_3$. Preliminary results show the usefulness of the techniques in studying these attached materials.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

233. PHOTOCHEMICAL ENERGY STORAGE: STUDIES OF INORGANIC PHOTOASSISTANCE — $130,000 — 01-01
Mark S. Wrighton
Department of Chemistry

Characterization, understanding, and improving the optical energy conversion efficiency of semiconductor-based photoelectrochemical cells are the objectives of this project. The surfaces of small band gap semiconducting photoelectrode materials such as Si, GaAs, and InP have been derivatized with ferrocene-based redox reagents to stabilize the n-type materials with respect to photoanodic decomposition and to improve kinetics for photooxidation of solution species. Most definitive data have been obtained for n-type Si showing that the derivatized Si is usable in H_2O solvent to photooxidize I^-, $Ru(NH_3)_6^{2+}$, and $Fe(CN)_6^{4-}$ that cannot be done reproducibly at the naked (non-derivatized) surface. P-type materials are under study as photocathodes for H_2 generation from H_2O. Surfaces of p-type materials such as Si and InP have been derivatized with an N,N'-dialkyl-4,4'-bipyridinium reagent as a prelude to studies aimed at improving H_2 evolution kinetics.

The following nine 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

234. PHOTOELECTROCHEMICAL STUDIES ON CHLORINS, PORPHYRINS AND THEIR METALLODERIVATIVES — $25,459 — 01-01
Alan D. Adler
Department of Chemistry

Improved preparations of synthetic chlorins and bacteriochlorins have been developed; also, simplified procedures for metallating the same. Initial voltammetric studies on these systems shows that aggregation effects in "pure" systems can modify the observed electrochemical behavior. Complex formation between unlike porphyrinoid structures further complicates the behavior of "mixed" systems. Strong photoeffects are seen on electrodes of low work function. While all this increases the experimental work needed to characterize these systems, it also demonstrates that they can serve as simple models for the natural photosynthetic systems, such as "active site" chlorophyll.

UNIVERSITY OF DELAWARE
Newark, Delaware 19711

235. PHOTOSENSITIVE MOLECULAR ARRAYS: A STUDY OF SYNTHETIC METHODS, PHOTOELECTRIC PROPERTIES, AND ENERGY TRANSFER MECHANISMS — $64,949 — 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 organizate 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.

UNIVERSITY OF SOUTHERN MISSISSIPPI
Hattiesburg, Mississippi 39401

236. PHOTOGALVANIC CELLS DRIVEN BY ELECTRON TRANSFER QUENCHING OF EXCITED SINGLET STATES $50,533 01-01
David Creed and Newton C. Fawcett
Department of Chemistry

The goal of this project is to develop more efficient photogalvanic cells for conversion of sunlight into electricity. The most efficient cells of this type have power conversion efficiencies of 0.03%, well below the theoretical maximum of about 20%. Several aspects of this problem are under study. The higher energy singlet states, rather than the triplet states, of the dyes are being investigated as the photochemically reactive species. Fluorescence quenching is used as a convenient handle on the bimolecular interactions of dye singlet states. Electrochemical and spectroscopic measurements of the formal potentials of the dye excited states are used to help in optimization of cell performance. The photogalvanic effect and the kinetics of the concurrent photochemical and thermal reactions are studied simultaneously in a crossed irradation beam and monitoring beam apparatus.

OHIO STATE UNIVERSITY
Columbus, Ohio 43210

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

The purpose of this project is to develop a solar battery using photosynthetic materials. Chloroplasts or Photosystem I particles isolated from chloroplasts are aspirated on to a filter. The filter is placed between two compartments, one of which contains the electron acceptor (flavin mononucleotide or anthroquinone sulfonate) and the other of which contains an electron donor [$K_4Fe(CN)_6$ or dichlorophenol-indophenol]. Electrodes are placed in each solution and the light-induced voltage is measured across a load resistance. The open circuit potential is 380-400 mV. The maximum short circuit current is 3 mA. 200 μW (1 W/m^2) are observed across a 300 Ω resistance using white light of 1000 W/m^2. We are presently testing the effects of varying electrode materials, donor/acceptor couples, cell design and chloroplast preparations on the power developed.

UNIVERSITY OF GEORGIA
Athens, Georgia 30602

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

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 reconversion 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.

UNIVERSITY OF GEORGIA
Athens, Georgia 30602

239. RESEARCH ON MICROEMULSIONS FOR SOLAR ENERGY STORAGE $40,000 01-01
Smith L. Holt
Department of Chemistry

Microemulsions are to be investigated for use in solar energy storage systems. In order to ascertain whether such solutions are of general utility, the exothermic conversion of quadricyclane to norbornadiene, catalyzed by the hydrocarbon insoluble tetra(para-sulfophenyl)porphinecobalt (II)anion, will be studied. Attempts will be made to microemulsify quadricyclane and factors affecting the stability of microemulsions will be investigated. The kinetics of the conversion process will be compared with the kinetics obtained with both homogeneous and supported catalyst systems. Removal of the water soluble catalyst from contact with the organic storage component will be attempted through thermally induced phase separation. The results should be applicable to any storage cycle which involves hydrophobic and hydrophilic components.

COLORADO STATE UNIVERSITY
Fort Collins, Colorado 80523

240. 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

Reversible, catalytic thermochemical reactions hold considerable promise for high-efficiency conversion of solar energy to a chemical form that can be transported and stored. Liquid phase Diels-Alder reactions are particularly well suited for such thermochemistry, since they are concerted, high-yield reactions with ΔH of 15-25 kcal/mol. A thorough understanding of component thermodynamics, reaction kinetics and physical parameters is essential for proper design of solar thermochemical systems. The goals of this project are to identify, in a systematic manner, promising liquid-phase Diels-Alder reactions. To date, several attractive Diels-Alder reactions have been identified, such as dimethyl esters of maleic and fumaric acid condensing with di-$\Delta^{1,1'}$-cyclopentene, di-$\Delta^{1,1'}$-cyclohexene and di-$\Delta^{1,1'}$-cycloheptene. Studies are now being undertaken to examine the quantitative effects of substituents on reaction ΔS, ΔH and activation energy (Ea). These experiments include equilibrium and kinetics studies of the effect of phenyl and isopropyl substituents on anthracene upon its condensation with maleic anhydride in solution (thus examining the internal entropy of rotation effect).

ARIZONA STATE UNIVERSITY
Tempe, Arizona 85281

241. ENHANCED SOLAR ENERGY COLLECTION IN PORPHYRIN BASED PHOTOCONVERSION SCHEMES $67,900 01-01
Thomas A. Moore and Devens Gust
Department of Chemistry

Although porphyrin based pigment systems are being used in a variety of solar energy conversion schemes, the absorption cross section of the porphyrin at the solar irradiance maximum is very low. Therefore, any system based on monolayers of porphyrin at a phase boundary only absorbs a small fraction of the incident sunlight. In natural photosynthetic membranes this problem is overcome by extensive use of accessory antenna pigments which transfer excitation energy to sites for conversion to useful chemical potential. The natural system is being mimicked by covalently attaching selected carotenoid pigments to porphyrins. The resulting carotenoporphyrins yield a large increase in the absorption cross section at the solar maximum with only a small increase in the area per molecule in a monolayer. Such antennas could be adapted for use in essentially any porphyrin based photoconversion scheme and could increase the yield of electrochemical potential energy based on incident sunlight by a factor of at least 80%.

CALIFORNIA STATE UNIVERSITY
Fullerton, California 92634

242. SOLAR ENERGY STORAGE VIA ENDOTHERMIC PHOTOCHEMICAL REACTIONS $57,741 01-01

John Olmstead, III and Carl C. Wamser
Department of Chemistry

The potential for solar energy storage of several unimolecular photoisomerization reactions is being investigated. The photoisomerizations of aromatic molecules to their Dewar analogues and the tran-cis photoisomerization about the aromatic azo linkage, both of which have previously been shown to have the potential for energy storage, 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. The possibilities are 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. The project involves three phases: synthesis of the compounds and systems to be studied, characterization of their photochemical products and quantum yields under sensitized and unsensitized conditions, and determination of the net endothermicities and storage efficiencies.

Chemical Physics

SRI INTERNATIONAL
Menlo Park, CA 94025

243. ENERGY TRANSFER STUDIES USING LARGE, HIGHLY VIBRATIONALLY EXCITED MOLECULES $64,000 01-02

J. R. Barker and G. P. Smith
Department of Chemical Kinetics

Experiments are being performed to study the energy-transfer properties of large molecules that are highly vibrationally excited. Excited molecules are prepared with known vibrational energies by excitation using a tunable pulsed laser followed by rapid internal conversion in the molecule. The time-dependent-thermal-lensing technique has shown that energy-transfer in gas-phase azulene is extremely rapid. Laser-excited fluorescence studies are underway to measure energy-transfer cross sections for various collision partners excited to various levels of internal excitation.

CORNELL UNIVERSITY
Ithaca, New York 14853

244. STUDIES OF THE COMBUSTION OF MODEL FUELS WITH LOW HYDROGEN CONTENT $55,000 01-02

Simon H. Bauer
Department of Chemistry

Our objectives are (a) to record chemical kinetics data on combustion, in the fuel-rich regime, of a selected sequence of model compounds which represent the primary components of fuels derived from non-petroleum sources; in particular, to determine conditions which lead to soot production; and (b) to develop a general, self-consistent analysis of the thermal fragmentation of these model molecular structures, and of the kinetics of attack of the fragments by oxidizers (O, O_2, OH). Preliminary pyrolysis data will be obtained with a 1" single pulse shock tube, under dilute conditions (with argon); analyses will be conducted primarily by gc-mass spec. We plan to ascertain the nature of the initial step in the pyrolysis, and to measure its rate constant, from laser-schlieren deflection by the post shock-front density-gradient. We will study the effects of additives on the density gradient profiles, with and without added oxygen, under fuel-rich conditions. Also, we hope to measure the dependence of soot production on the fuel-oxygen ratio. This can be most easily followed in a 2" shock tube, instrumented with a four watt argon ion laser for light scattering measurements.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

245. FINITE-TIME THERMODYNAMICS $60,000 01-02
R. Stephen Berry
Department of Chemistry

Conventional thermodynamics establishes bounds for heat and work exchanges based on reversible, infinitely slow processes. More realistic bounds can be established when the constraints on the processes include constraints on time or rate. This research is an exploration of the effects of finite-time constraints on optimal processes. Comparisons are made of the consequences of different criteria of optimality, such as maximum efficiency, maximum effectiveness, maximum power and minimum entropy production. In many cases, it is possible to determine the process that would yield the optimal solution, and thus to provide guidance to designers of devices. Systems under study include heat engines, separation processes and chemical process systems.

COLUMBIA UNIVERSITY
New York, New York 10027

246. ENERGY PARTITIONING IN ELEMENTARY GAS PHASE REACTIONS $66,000 01-02
Richard Bersohn
Department of Chemistry

Atoms with kinetic energy distribution are generated by photodissociation. These atoms are reacted with a diatomic molecule BC and the final internal state distribution P(v,J) of the product AB probed by laser induced fluorescence. It is hoped to study four three-center reactions of this type and one four-center reaction:

		ΔE(kcal/mole)
1)	$O(^1D) + H_2 \rightarrow OH + H$	-44
2)	$C(^3P) + NO \rightarrow CN + O(^3P)$	-25
3)	$C(^3P) + O_2 \rightarrow CO + O\ (^3P,\ ^1D \text{ or } ^1S)$	-138
4)	$S(^1D) + O_2 \rightarrow SO + O(^3P)$	-33
5)	$C(^3P) + SO_2 \rightarrow CO + SO\ (X^3\Sigma)$	-125

and in every case to determine P(v,J) for the product diatomic(s).

STATE UNIVERSITY OF NEW YORK/BUFFALO
Buffalo, New York 14214

247. INTRACAVITY ABSORBER EFFECTS IN A CW DYE LASER — $54,000 — 01-02
G.O. Brink
Department of Physics and Astronomy

Dye laser intracavity absorption is being studied as a technique for doing spectroscopy on low density atoms, molecules and ions. A new model of the process has been developed based on an analogy between a multimode dye laser and a superregenerative oscillator. This model is able to account for the observed line shape at least at high absorber densities. At low densities an enhancement effect occurs which has not as yet been explained. To date densities of about $10^6/\mathrm{cm}^3$ have been detected by absorption and $10^4/\mathrm{cm}^3$ detected by enhancement. The line shape has also been observed to be a function of the scan rate of the dye laser, and this is presently attributed to a forced quenching of a given laser mode. Work is continuing in an effort to understand the many complex phenomena associated with dye laser intracavity absorption.

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

248. UNIMOLECULAR DECAY DYNAMICS OF INTERNAL ENERGY SELECTED MOLECULES — $55,000 — 01-02
F. Fleming Crim
Department of Chemistry

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. The detection schemes (visible chemiluminescence and laser induced fluorescence) directly measure unimolecular decay rates and, in the second case, yield information on the final energy content of the fragments. The highly specific excitation provides a means of exploring the influence of different initial vibrational excitations on unimolecular decay rates, and state resolved detection reveals features of the dynamics which control energy partitioning among product degrees-of-freedom.

RICE UNIVERSITY
Houston, Texas 77001

249. INFRARED ABSORPTION SPECTROSCOPY WITH COLOR CENTER LASERS $54,000 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. Two absorption spectroscopy methods utilizing these lasers are being developed. One is a technique for balancing out source noise using the magnetic rotation effect. The absorption spectrum of the free radical OH has been observed using this technique and work is in progress to extend observations with this technique to other free radicals such as HO_2 and NH_2. The second method being developed is aimed at situations where Zeeman modulation is not possible and uses frequency modulation of the source with the molecular absorption serving as a discriminator. It is expected that the phase modulation obtainable with an electro-optic crystal will provide a means of introducing the source frequency modulation without interfering amplitude modulation.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

250. LASER PHOTOELECTRON SPECTROSCOPY OF IONS $50,000 01-02
G. Barney Ellison
Department of Chemistry

This program is centered on the experimental study of the photoelectron spectroscopy of negative ions. Mass-selected ion beams are intersected with an argon ion laser operating on a single line (λ = 488 nm). The photodetached electrons are energy-analyzed with a hemispherical electrostatic analyzer and counted. This type of ion spectroscopy provides accurate electron affinities for a number of reactive molecules related to combustion studies. These ions include alkoxides (RO^-), carboxylates ($RCOO^-$), and hydroperoxides (ROO^-).

UNIVERSITY OF CALIFORNIA
Los Angeles, California 90024

251.	TIME RESOLVED RESONANCE RAMAN AND ENERGY TRANSFER STUDIES ON BACTERIORHODOPSIN AND OTHER PHOTOCHEMICAL SYSTEMS M. A. El-Sayed Department of Chemistry	$77,800	01-02

Time resolved resonance Raman techniques have been developed to determine the vibrational spectra of transients in the picosecond time scale. Structural information can thus be deduced from the vibrational spectra of these very short lived species. The knowledge of these structures is vital to our understanding of the mechanisms of important photobiological functions, e.g., the photosynthesis in bacteriorhodopsin and the photodissociation of carbon monoxide hemoglobin.

UNIVERSITY OF OREGON
Eugene, Oregon 97430

252.	LASER SPECTROSCOPY OF COMBUSTION INTERMEDIATES P. C. Engelking Department of Chemistry	$78,700 24 mo. FY79-80	01-02

The electronic spectra of molecular radicals are being measured by laser induced fluorescence techniques in a fast flow system. The identification and characterization of molecular radical spectra allows one to understand the internal structure of molecular radicals, and also provides the needed spectroscopic information basic to the detection and identification of these combustion intermediates by laser techniques in actual flame environments. Radicals chosen for this study such as methoxyl CH_3O, and other alkoxyl species, have importance as chemical intermediates in combustion reactions. They are being studied in an inert gas, fast flow system, which besides providing this basic spectroscopic information, permits measurement of some of their chemical reaction rates by the effect of chemical reagents upon the observed laser induced fluorescence of the radicals.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

253. INFRARED LASER INDUCED ORGANIC REACTIONS $46,300 01-02
William E. Farneth
Department of Chemistry

This project investigates the potential and present utility of high power infrared lasers for initiating and directing chemical reactions of organic molecules. Both homogeneous gas phase systems, and heterogeneous gas/solid systems are under investigation. In both cases experiments designed to define the ground rules under which chemical applications of the IR multiphoton activation will be constrained to operate have been undertaken. For example, the homogeneous chemistry involves excitation of small ring compounds, cyclopropanes and oxetanes, and observation of decomposition yields and branching ratios as a function of laser intensity, frequency, reactant pressure and bath gas composition. These experiments are yielding information about intermolecular and intramolecular energy distributions among reacting molecules. The heterogeneous system currently under investigation is Br_2 or haloethylenes over graphite. Chemical modifications in both the vapor and the solid are being monitored as a function of experimental geometry, laser power and reactant pressure and structure.

UNIVERSITY OF ROCHESTER
Rochester, New York 14627

254. MOLECULAR BEAM STUDIES OF ION-NEUTRAL COLLISIONS $51,000 01-02
James M. Farrar
Department of Chemistry

The fundamental goals of this research are to study the dynamics of elementary chemical reactions among ions in the gas phase and reactions of highly reactive neutrals, such as free radicals, which ultimately produce ions. Low energy proton transfer and charge transfer reactions of H_2^+ with the rare gases, diatomics such as N_2, O_2, and CO, and polyatomics such as H_2O are being studied by the crossed molecular beam technique. The resultant angular and energy distributions of reaction products are being interpreted in terms of recent theory on the structures of appropriate potential surfaces and dynamics calculated on such surfaces. Proton transfer reactions of HCO^+ to H_2O and hydrocarbons are being studied. Techniques for the production of clean beams of CH radicals are being developed, with the goal of studying elementary associative ionization reactions of CH with O and unsaturated hydrocarbons such as C_2H_2; such reactions are thought to be important ion producers in hydrocarbon flames.

AEROCHEM RESEARCH LABORATORIES, INC.
Princeton, New Jersey 08540

255. EXPERIMENTAL DETERMINATION OF RATE COEFFICIENTS FOR IMPORTANT COMBUSTION/FUEL CONVERSION REACTIONS BY A NOVEL HIGH-TEMPERATURE PHOTOLYSIS TECHNIQUE $82,000 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 benchmark reaction of oxygen atoms with methane over the 125 to 1330°C range provide the first continuous data set available in this regime and are consistent with previous measurements at the extremes. Reaction of hydroxyl radical with benzene is now being investigated with particular emphasis on temperatures above 750°C where no prior measurements have been made. Subsequently, studies of the reactions of methyl radicals with oxygen molecules and atoms will be initiated.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

256. REACTIONS OF IONS WITH ATOMIC AND MOLECULAR FREE RADICALS $48,000 01-02
W. R. Gentry
Department of Chemistry

The reactions between molecular ions and atomic free radicals are interesting as examples of processes in which multiple low-lying electronic states of the intermediate species play an important role. However, because of technical difficulties, very few such reactions have been observed. The unique University of Minnesota merged molecular beam facility has made possible direct measurements of the microscopic reaction cross sections for several of the most fundamental of these reactions, over the range of kinetic energy from 0.001 eV to 30 eV. Studies have recently been completed for the reactions of H_2^+ with C, N, O and F atoms, and future investigations will deal with more complicated processes, such as $NH^+ + O \rightarrow NO^+ + H$, in which angular momentum effects are expected to provide significant dynamical constraints.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

257. REACTION MECHANISMS IN COMBUSTION: FORMATION OF SOOT AND POLYCYCLIC AROMATIC HYDROCARBONS — $56,000 — 01-02
William A. Goddard III

We are studying the microscopic mechanisms of the gas phase and heterogeneous processes involved in the formation of soot and polycyclic aromatic hydrocarbons (PCAH). 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 in the formation of PCAH. 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.

UNIVERSITY OF ILLINOIS AT CHICAGO CIRCLE
Chicago, Illinois 60680

258. MEASUREMENT OF GAS PHASE REACTION RATE CONSTANTS — $53,000, 15 mo. — 01-02
Robert J. Gordon
Department of Chemistry

The objective of this project is to measure the rate constants of two types of chemical processes: the reactions of atoms with small molecules and the vibrational relaxation and chemical reactions of ozone with various molecules. For the first part, a temperature controlled flash photolysis - resonance fluorescence apparatus is operational and preliminary measurements of Cl + H_2, D_2 and CH_3Br are being made. A complete study of the abstraction, exchange, and reverse reactions of Cl + H_2 and Cl + D_2 is under way. In the second study the rate of vibrational relaxation of ozone by H_2O and D_2O is measured in a fast flow apparatus. An anomalous negative temperature dependence for both molecules and an inverse isotope effect are explained in terms of a metastable complex model of energy transfer. Also being investigated is the reaction of NO + O_3 in a large capacity flow reactor built for this study.

GEORGE WASHINGTON UNIVERSITY
Washington, D. C. 20052

259. CHARACTERISTIC PARAMETERS IN COMBUSTION PROCESSES AND THEIR ACCESSIBILITY TO CURRENT AND FUTURE DIAGNOSTICS — $22,000 — 01-02
R. Goulard
School of Engineering and Applied Science

Current combustion research shows a growing awareness of the potential offered by the new high speed three-dimensional techniques. Recent advances in the fluid dynamics of jet mixing emphasize the 10 KHz range (especially vortex shedding). Also the very fast subnanosecond range of radical kinetics are in the time range of the comparably fast scattering and fluorescence processes. High speed diagnostics are discussed in these two ranges of time resolution, with an emphasis on optical tomography for the fluid dynamic time range (10^{-4} sec) and on picosecond techniques for the physical chemistry range (10^{-9} sec). Multi-element sensors, especially in the visible range, have the capability to respond at a 2 MHz rate per element, which allows time for charge shifting, analog-to-digital conversion, and processing of a 100-element set within the fluid dynamics time. Similarly mode locking lasers and streak cameras offer the possibility of picosecond range chemical diagnostics.

BROWN UNIVERSITY
Providence, Rhode Island 02912

260. INTERACTIONS OF MOLECULES WITH SURFACES — $62,000 — 01-02
E. F. Greene
Department of Chemistry

The aims of this work are to show how molecules interact with surfaces in three particular experiments. In one, a beam of krypton atoms is scattered from a graphite surface and only those atoms leaving with little change in speed are recorded. The results, interpreted using a simple model, should help to probe the structure of the surface. In another experiment the surfaces of metals, semiconductors, and insulators are exposed to beams of alkali atoms and the yields of reflected atoms and ions measured. The nature of the surface is monitored with low energy elelectron diffraction and Auger equipment. The results show how atoms interact with surfaces. In the third experiment, reactions are caused to occur when fast molecules are suddenly brought to rest by collision with a surface. There is a minimum kinetic energy below which molecules of tungsten hexacarbonyl fail to react, and this minimum is only weakly dependent on their internal energy. Comparison of the results with those from thermal reactions may show how violent collisions can change the paths reactions take.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

261. INFRARED LASER-INDUCED COMBUSTION AND FLAME PROCESSES $55,000 01-02
William A. Guillory
Department of Chemistry

The objective of this project is to obtain an indepth understanding of elementary physical and chemical processes occurring in flame and combustion systems. This objective is accomplished by the study of energy transfer processes, state-to-state bimolecular reactions of important flame components, and the characterization of hydrocarbon combustion. The unique aspect of these studies is that the simulated flame and combustion processes are initiated by infrared multiple photon absorption from a high power carbon dioxide laser; with subsequent diagnostics being performed by due laser-induced fluorescence, visible and infrared emission, and routine analytical techniques. Presently under investigation are the experimental and theoretical energy transfer dynamics of propynal under collisional and collisionless conditions, bimolecular reactions of CH and C_3 with O_2 and NO, and the combustion of propylene, propane, and propenal.

ILLINOIS INSTITUTE OF TECHNOLOGY
Chicago, Illinois 60616

262. STUDIES OF COMBUSTION KINETICS AND MECHANICS $60,000 01-02
D. 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. The facility is now being used to study the reactions of allyl (C_3H_5) radicals. The reactions of C_3H_5 with NO, Br_2, Cl_2, O_2 and C_3H_5Br (the C_3H_5) precursor) are being studied. A large number of potential sources of other free radicals are being tested to identify suitable precursors for studies of the reactions of other polyatomic free radicals important in combustion.

STANFORD UNIVERSITY
Stanford, California 94305

263. COMBUSTION GAS MEASUREMENTS USING TUNABLE LASER ABSORPTION SPECTROSCOPY $59,000 01-02
R. K. Hanson
Department of Mechanical Engineering

Objectives of this research are: (1) the development of tunable laser absorption spectroscopy as a technique for measuring species concentrations in combustion flows, with emphasis on pollutant species; and (2) the measurement of fundamental spectroscopic parameters (band strengths and collision-broadened linewidths) of critical combustion species at combustion conditions. A tunable cw diode laser is employed for infrared absorption spectroscopy and a tunable cw ring dye laser is used for absorption spectroscopy at uv and visible wavelengths. The experimental procedure involves modulating the wavelength of the narrow-linewidth laser to record fully resolved absorption line profiles of vibration-rotation or electronic transitions. Current experiments with the diode laser include band strength and collision-broadened linewidth measurements of CO and NO in a room temperature absorption cell, in the post-flame region of a flat flame burner and in a shock tube. Tunable dye-laser experiments are aimed at measuring Na concentrations and collision-broadened linewidths.

STANFORD UNIVERSITY
Stanford, California 94305

264. THE KINETICS OF SOME REACTIONS OF HCN AT HIGH TEMPERATURES $54,000 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, D. C. 20059

265. LASER STUDIES OF THE DYNAMICS OF ATOM-MOLECULE REACTIONS $44,000 01-02

William M. Jackson
Department of Chemistry

The objectives of this work are to measure the quantum state distribution of free radical fragments produced in atom-molecule reactions. This information is important in understanding both the energy balance in combustion processes and the dynamics of chemical reactions. We are also investigating the use of the combination of an ArF laser and a molecular beam as a means for studying atom-radical reactions. This information will aid in understanding the energy balance in combustion processes, the reactions leading to atmospheric NO_x, and provide fundamental information about the dynamics of chemical reactions. Carbon atoms are produced by the vacuum ultraviolet photolysis of C_3O_2 and are reacted with NO or N_2O. These reactions are exothermic by 1.1 and 2.6 e.v. respectively. The quantum state distribution of the resulting CN radicals are determined by laser induced fluorescence. The results indicate that some of the excess energy is used to rotationally and vibrationally excite the CN fragment. Other schemes for producing combustion related species in a molecular Beam via ArF multiple photon and multiphoton processes are being investigated.

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

266. HIGH RESOLUTION INFRARED SPECTROSCOPY: DISCRETE STATES IN THE QUASICONTINUUM $54,000 01-02

Kenneth C. Janda
Department of Chemistry

The goal of this project is to understand the nature of intramolecular energy redistribution in vibrationally excited molecules. Three techniques are being developed to obtain high resolution spectra of such molecules: 1) photodissociation spectroscopy of van der Waals species, 2) infrared laser-induced fluorescence, and 3) infrared-optical double resonance. The photodissociation of $(C_2H_4)_2$ by low power, continuous 950 cm^{-1} radiation from a CO_2 laser indicates that the predissociative state has a lifetime of 0.3 psec. Work is in progress to measure lifetimes of states with C-H stretching modes excited at ~3000 cm^{-1}. Also, a case for low power IR isotope separation using BCl_3 is being attempted. The infrared fluorescence and infrared-optical double resonance are being implemented so that excited vibrational states of stable molecules may be studied.

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

267. MULTIPHOTON DISSOCIATION SPECTROSCOPY AND PHOTOCHEMISTRY $50,000 01-02
Philip M. Johnson
Department of Chemistry

This research will develop 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 will be measured by using multiphoton ionization or fluorescence to detect the photoproduct. This will produce a multiphoton dissociation spectrum which will provide information about the relative decomposition pathways and the vibronic structure of excited states which decompose. These spectra will be valuable and complementary supplements to multiphoton ionization spectra for the understanding of excited molecular states. Absolute photochemical rates will be determined by use of the kinetic framework of multiphoton ionization. The techniques will be 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

268. IDENTIFICATION AND TEMPORAL BEHAVIOR OF RADICAL INTERMEDIATES FORMED DURING THE COMBUSTION AND PYROLYSIS OF GASEOUS FUELS: KINETIC PATHWAYS TO SOOT FORMATION $46,000 01-02
Ralph D. Kern, Jr.
Department of Chemistry

The formation of soot is a major problem in the combustion of synthetic fuels that contain an abundance of aromatic compounds. The kinetic pathways to the polymers of carbon from a key aromatic compound, toluene, are being investigated by heating specified amounts of toluene to known temperatures and pressures in a shock tube. The gas from the reflected shock zone is sampled dynamically during the course of the reaction by a time-of-flight mass spectrometer. The identity, quantity, and time history of the important intermediates leading to soot formation are essential data that are required for the understanding of the mechanism of soot formation and its ultimate control. Initial results indicate the preponderance of decomposition pathways over ring condensation routes. This observation is of consequence to previous work which reported extremely high conversions of parent fuels to soot in pyrolytic and combustion systems.

Chemical Physics, continued

UNIVERSITY OF ILLINOIS/CHICAGO CIRCLE
Chicago, Illinois 60680

269. LASER-SCHLIEREN, SHOCK TUBE STUDIES OF HIGH-TEMPERATURE HYDROCARBON PYROLYSIS RATES $49,000 01-02
John H. Kiefer
Department of Energy Engineering

The primary purpose of this project is elucidation of various facets of the pyrolysis mechanism for several fuel hydrocarbons. The initial studies involve propane, ethane, and the butanes, but extension to aromatics is anticipated. The technique used is a combination of the shock tube with laser-schlieren measurement of the density gradient generated by endothermic decomposition. Overall, the pyrolysis of these fuels is complex, but the direct measurement of rate afforded by this technique, together with its exceptional resolution, allows at least a partial separation of the initial dissociation. This resolution also allows determination of very fast rates so the accessible temperature range can be considerably extended. Thus the expected results are determination of an unambiguous rate constant for the primary dissociation step and extension of such measurements to the temperature range of greatest interest in combustion.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

270. MEASUREMENT OF RADICAL SPECIES CONCENTRATIONS IN FLAMES BY FLUORESCENCE AND ABSORPTION USING A TUNABLE DYE LASER $79,800 01-02
Normand M. Laurendeau and Donald W. Sweeney
School of Mechanical Engineering

The goal of this project is the development of a reliable fluorescence technique to measure the concentrations of radical flame species. Saturated fluorescence is a particularly promising method because, at saturation or near saturation conditions, the fluorescence signal becomes much less dependent on collisional quenching processes. A new fluorescence model is proposed. The balanced cross-rate model is relatively simple and applicable over a wide range of flame conditions. It is particularly appropriate for the case where the laser excitation pulse is so short that rotational steady state is not established. Preliminary saturated fluorescence measurements of OH have been performed in a one atmosphere methane-air touch. Fluorescence is induced by a high intensity, few nanosecond pulse from a Nd:YAG-pumped dye laser. The fluorescence spectrum is analyzed by using a grating spectrometer; the fluorescence signal is time-resolved by using a fast photomultiplier and sampling oscilloscope.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

271. THEORETICAL STUDIES ON HETEROGENEOUS COMBUSTION $45,000 01-02
C. K. Law
Department of Mechanical and Nuclear Engineering

The objective of this project is to understand the fundamental heterogeneous physico-chemical processes governing the vaporization, ignition, combustion, and extinction of fuel spray jets in hot-oxidizing environments simulating the interior of practical combustors. An explicit universal ignition criterion for fuel droplets in sprays has been derived; its incorporation in spray modeling is straightforward. It has also been shown that the classical d^2-Law of droplet combustion neglects the important transient process of fuel accumulation in the region interior to the droplet flame and therefore may grossly over-estimate the chemical heat release rate. A revised theory has since been formulated; its predictions agree well with existing experimental results. The dynamics and vaporization of a round spray jet is currently being modelled. Of particular interest here is the comparison of the rates of oxidizer entrainment and droplet vaporization in deciding the ignitability of individual droplets.

UNIVERSITY OF CALIFORNIA/IRVINE
Irvine, California 92717

272. INTRAMOLECULAR ELECTRONIC ENERGY TRANSFER PROCESSES $64,000 01-02
Edward K. C. Lee
Department of Chemistry

The basic aim of this research project is to understand the dynamics of energy flow in molecules. Small molecules are selectively excited to well characterized rotational, vibrational, and electronic states, and their evolution in terms of radiative decay, intramolecular energy redistribution, intermolecular energy transfer, excimer formation, and chemical reactions are being studied. Sulfur dioxide, formaldehyde and glyoxal are under investigation by time-resolved fluorescence emission spectroscopy following laser excitation for measuring rates of rotational, vibrational and electronic energy transfer and further by Fourier transform infrared spectroscopy for measuring photolysis products in low temperature matrices. It was found that collisional rotational relaxation in the photoexcited SO_2 proceeds by dipole mechanism.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

273. STUDIES OF FREE RADICALS BY ULTRAVIOLET EXCIMER LASER PHOTOLYSIS Stephen R. Leone Department of Chemistry	$43,000	01-02

A new technique is being developed to study the spectroscopy, energy transfer, and reactivity of free radicals containing high vibrational excitation. Experiments on radicals such as CH_2I, obtained by laser photolysis of CH_2I_2, are providing a tremendous amount of new data on the rates of vibrational relaxation and spectroscopy of highly excited free radical species. These studies are being extended to the CH_3 radical, because of its fundamental importance to combustion systems. A laser-initiated chain reaction method is used to make realtime kinetic analyses of combustion reactions. The complete mathematical formalism is verified experimentally on several well-known and new chain systems. These methods are used to analyze chain reactions which proceed by very slow mechanisms and which contain unique aspects of termination and propagation.

KANSAS STATE UNIVERSITY
Manhattan, Kansas 66506

273a. DIFFUSION FLAME STUDIES OF THE CHEMICAL AND PHYSICAL MECHANISMS OF SOOT FORMATION FROM AROMATIC AND SUBSTITUTED AROMATIC FUELS T. W. Lester, J. F. Merklin, and C. M. Sorensen Departments of Nuclear Engineering and Physics	$50,000	01-02

The chemical mechanisms of soot formation from aromatic and substituted aromatic hydrocarbons will be studied. A laminar, conical, diffusion flame, supported by either carbon monoxide or hydrogen burning in air and doped with aromatic, substituted aromatic, aromatic with sidechains, and aliphatic hydrocarbons will be used in the investigation. Sampling for stable species will be conducted with a microquartz probe and with both gas chromatographic and mass spectrometric analysis. Our intent is to discern whether ring stability is important in maximizing the yield of soot. Further, the nature of the chemical mechanism, whether free radical or molecular, will be determined over a wide range of pyrolysis zone temperatures. The use of a powerful new technique, photon correlation spectroscopy, is proposed to map the soot number density and size distribution.

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

274. LUMINESCENT SPECTRA IN ION-NEUTRAL COLLISIONS $59,000 01-02
Jacob J. Leventhal
Department of Physics

This research is directed toward understanding the mechanisms of energy transfer and energy conversion in atomic and molecular interactions. Diagnosis is accomplished by observing luminescence resulting from decay of energetically excited products of the interaction and by detecting ionic species resulting from the interaction. These data yield detailed information on the partitioning of internal energy among the available quantum states of the products and the preferred reaction channels for a given system. Several different types of reacting molecular systems, that is, ion - atom, atom - atom, atom - molecule, etc. Preparation is underway to permit study of processes involving energetically excited reactant atoms or molecules. Excitation is to be accomplished with a tunable dye laser.

UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

275. EXPERIMENTAL STUDIES OF THE IONIZATIONS AND BONDING OF SMALL MOLECULES ATTACHED TO TRANSITION METALS $60,000 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.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

276. LASER INDUCED CHEMICAL REACTIONS AND LASER-COLLISION PROCESSES $54,000 01-02
John C. Light
Department of Chemistry

There now exist lasers powerful enough to affect the dynamics of atomic and molecular collisions in the gas phase. These processes differ from those observed when collision partners are prepared (by lasers) in specific internal states before collision, in that the photon field couples different states during the collision processes. Model systems were used to estimate the effects of non-resonant radiation on atom-diatom reactions and the effects of collisions on the absorption of infrared radiation within a vibration-rotation manifold. For fields on the order of 10^8-10^{10} W/cm^2 these effects become prominent, and apparently have been observed with small probability at much lower fields. In addition an exact (and efficient) quantum method has been developed for polyatomic dissociation. Fano-type resonance structure in the probability versus frequency plots for specific initial and final states (model $CO_2(v,j) + h\nu \rightarrow O + CO(v',j')$) has been predicted. These studies will be extended to more realistic 3-D systems and to multiphoton processes.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

277. ELECTRONIC RELAXATION PROCESSES IN POLYATOMIC MOLECULES $56,000 01-02
E. C. Lim
Department of Chemistry

The purpose of this research is to utilize isotope, solvent, substituent, temperature and excitation energy dependence of radiationless transitions in polyatomic molecules to elucidate the dynamics of electronic and vibrational relaxation. The isotope, temperature and solvent dependence of fluorescence and singlet → triplet intersystem crossing in several nitrogen-heterocyclic (quinoline, isoquinoline, etc.) and aromatic carbonyl compounds (thioxanthone, pyrene-3-aldehyde, etc.) reveal the occurrence of an important $S_1 \rightarrow S_0$ internal conversion due to "proximity effect", while the excess vibrational energy dependence of $T_1 \rightarrow S_0$ intersystem crossing in gas-phase aromatic carbonyls (benzaldehyde, phenyl alkyl ketones, etc.) provides a useful probe of intramolecular vibrational relaxation. The position-dependent isotope effects on nonradiative decay rate of electron donor-acceptor complexes are being investigated to deduce C–H hyperconjugation in alkyl benzene cations.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

278. MOLECULAR BEAM STUDIES OF METASTABLE RARE GAS CHEMILUMINESCENT REACTIONS $47,000 01-02
R. 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 chemiionization 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 eximer and excitation transfer lasers.

PRINCETON UNIVERSITY
Princeton, New Jersey 08544

279. DYNAMICAL STUDIES OF MOLECULAR SYSTEMS $62,500 01-02
Herschel Rabitz
Department of Chemistry

This research concerns the study of chemical kinetics, relaxation phenomena, and related molecular collision problems. A central part of the research involves the determination of critical parameter dependencies in chemical kinetics and molecular collisions. This goal is being achieved by the development and application of new sensitivity analysis methods capable of probing the complex interactions in these problems. A natural extension of this work involves the study of macroscopic kinetic relaxation phenomena. In this case, theoretically derived scaling relations are being utilized to invert molecular relaxation experiments and spectral lineshapes to their underlying kinetic information. Collisional interactions are a common touch point for all of these studies and we are pursuing the development and application of new techniques for the practical calculation of collision events. This work involves the study of both analytical models as well as the development of new numerical techniques.

CALSPAN ADVANCED TECHNOLOGY CENTER
Buffalo, New York 14225

280. VIBRATIONAL ENERGY TRANSFER KINETICS IN MOLECULAR DISEQUILIBRIUM — $55,331 — 01-02
J. William Rich
Physical Sciences Group

This program is an experimental study of the chemical kinetics of gaseous molecular systems under conditions of extreme disequilibrium of the vibrational energy modes. 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. High steady-state excitation of the CO vibrational mode (0.3 eV/molecule) is achieved, while a translational-rotational temperature near 300°K is maintained by the steady flow of cold gas into the 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; these states have energies up to 8 eV, which is 75% of the CO dissociation energy. Under these conditions, the carbon monoxide reacts to form vapor phase C_2 and CO_2; the carbon thus produced is enriched in ^{13}C. In a separate series of experiments, cyanogen, $(CN)_2$, has been synthesized by excitation of CO/N_2 mixtures. Research is concentrating on mapping the detailed mechanism of these reactions, by use of emission spectroscopy and mass spectrographic diagnostics.

STANFORD UNIVERSITY
Stanford, California 94305

281. THEORY OF CHEMICAL KINETICS — $75,000 — 01-02
John Ross
Department of Chemistry

Progress has been made in the theory of chemical kinetics in the following areas: In chemical dynamics we have studied the basis of the sudden approximation and have developed a consistent perturbation theory based on multiple time scales. The work is applicable to inelastic and reactive collisions. In the area of chemical instabilities we have studied the interaction of hydrodynamic instabilities with chemical reactions in the Bénard geometry. We have investigated the efficiency of chemical reactions for heat engines in which the fluid is not at equilibrium. In the case of oscillatory systems for the working fluid we find resonance effects and have applied this concept to an analysis of glycolysis which is the conversion of energy from sugar to ATP. The efficiency of this free energy conversion, if done in an oscillatory mode, is increased over that of the stationary state operation.

WRIGHT STATE UNIVERSITY
Dayton, Ohio 45435

282. THE DIRECT DETERMINATION OF ATOM AND RADICAL CONCENTRATIONS IN THERMAL REACTIONS OF HYDROCARBONS AND OTHER GASES $45,180 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 spectroscopy in the vacuum ultraviolet. Calibrations for O are made by measurement of the profiles of the lines emitted by the discharge lamp and empirically by producing O atoms in the shock tube by dissociation of N_2O. Measurements of H and O atom concentrations lead to kinetic data for combustion of hydrogen, methane, ethane and propane. Energy transfer efficiencies to reacting molecules are also studied and compared to theoretical predictions.

RICE UNIVERSITY
Houston, Texas 77001

283. HYPERSONIC BEAM LASER PHOTOLYSIS $54,000 01-02

R. E. Smalley
Department of Chemistry

The primary object of this research is to develop a powerful new technique for the detailed spectral study of free radicals, diradicals, and other reaction intermediates cooled to near absolute zero in a hypersonic beam. These highly reactive species are produced by laser photolysis of a suitable precursor molecule seeded in a hypersonic free jet of helium. Using a newly developed pulsed nozzle apparatus capable of operating at 20 atmospheres with a 0.1 cm diameter orifice fully opened in 50 microseconds, extremely intense pulsed jets have been produced. Radicals produced by photolysis in the early regions of these jets are cooled in the subsequent expansion to record low temperatures. The absorption spectrum of these ultracold radicals is then monitored at high resolution by any of a number of techniques, including laser-induced fluorescence excitation, resonant two-photon ionization (R2PI), or photofragment generation. Recently the methylene radical (CH_2) has been produced in such a hypersonic jet by photolysis of ketene.

UNIVERSITY OF CALIFORNIA
Santa Barbara, California 93106

284. LASER FLUORESCENCE STUDIES OF THE DETAILED COMBUSTION OF NITROGEN AND SULFUR BEARING FUELS $55,000 01-02
M. Steinberg, K. Schofield, and D. O. Harris
Quantum Institute

The basic objectives of this project are the identification of the dominant chemistry involved in NO formation from fuel nitrogen in fuel rich flames, the analysis of the NO_x/SO_x interaction chemistry in these flames, and an examination of the roles of CH and C_2 in the NO_x and SO_x cycles. Quantitative laser induced fluorescence techniques are being developed and employed to monitor the time varying concentrations of OH, NO, NO_2, CN, HCN, NH, and NH_2 in a series of $H_2/O_2/N_2$ and $C_2H_2/O_2/N_2$ flames of varying compositions and temperature, to which NH_3, CH_3NH_2, H_2S, or SO_2 are added as dopants. The measured concentration profiles, along with previous data for S_2, SH, SO, and SO_2, are analyzed to generate detailed models for the coupled chemistry in the systems studied.

UNIVERSITY OF CALIFORNIA/SAN DIEGO
La Jolla, California 92093

285. SHOCK-TUBE STUDIES OF IMPORTANT COMBUSTION-REACTION STEPS INVOLVING METHYL RADICALS $55,000 01-02
Klaus G. P. Sulzmann
Energy Center

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 O_2, O, H, OH, etc. The methyl radicals are produced behind reflected shock-waves in argon-diluted mixtures containing $(CH_3)_2CO_2$ 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 CH_3, O, H, CH_2 and CH_3O, as well as by infrared emission techniques for CO_2 and H_2CO. The results are used to define important elementary reaction paths governing the fate of CH_3. 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.

Chemical Physics, continued

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

286. VARIATIONAL TRANSITION STATE THEORY $37,000 01-02
Donald G. Truhlar
Department of Chemistry

Several projects involving variational transition state theory are being pursued. Applications and tests are being carried out for kinetic isotope effects and reaction rates of several systems, including $F + H_2$, $H + F_2$, $Cl + H_2$, $Cl + HCl$, and $O + H_2$. In addition improvements in the theory are being attempted and the formalism is being extended to treat a more complicated class of reactions.

NATIONAL BUREAU OF STANDARDS
Washington, D. C. 20234

287. KINETIC DATA BASE FOR COMBUSTION MODELING $72,000 01-02
Wing Tsang and R. F. Hampson
Chemical Kinetics Division

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.

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

288. A KINETIC STUDY OF RADICAL-AROMATIC HYDROCARBON REACTIONS $50,000 01-02

F. P. Tully and 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 and pyrolysis chain step reactions O(OH,H) + 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.

STANFORD UNIVERSITY
Stanford, California 94305

289. ENERGY DISTRIBUTION OF PHOTOFRAGMENTS RESULTING FROM IR MULTIPHOTON DISSOCIATION $55,000 01-02

Richard N. Zare
Department of Chemistry

The main objective of this research program is to further our understanding of infrared multiphoton dissociation, whereby a polyatomic molecule in an intense radiation field of a pulsed infrared laser (CO_2) undergoes unimolecular decay. We will concentrate on the measurement of the detailed energy content of the fragments. This will be determined from the fragment's unrelaxed excitation spectrum, using the method of laser fluorescence analysis. During this period we will construct a well-characterized CO_2 laser source so that the effect of pulse shape, pulse duration, frequency, fluence, intensity, etc. can be assessed. Experiments will be carried out both in the collisionless environment of a molecular beam and in the collisional environment of a low-pressure bulb. The time-resolved laser-induced fluorescence of the fragments will be recorded subsequent to the photolysis pulse so that the temporal evaluation of the energized parent molecule might be followed. The above state-to-state information will be used to construct models for the IR multiphoton dissociation process.

UNIVERSITY OF PITTSBURGH
Pittsburgh, Pennsylvania 15260

290. CHARGE EXCHANGE COLLISIONS OF HIGHLY STRIPPED IONS WITH ATOMIC HYDROGEN $69,400 01-03
J. E. Bayfield
Department of Physics and Astronomy

The development of decelerated highly stripped ion beams is continuing, with emphasis upon high charge state purity and narrow energy spread. A sequence of charge exchange cross section measurements continues to concentrate upon carbon and oxygen ions. A new channel-plate position sensitive ion detection system is being tested and should increase cross section data acquisition rates an order of magnitude or more. The atomic collision cross sections under study are needed to assess impurity radiation loss mechanisms and auxiliary neutral beam plasma heating effectiveness in magnetic fusion devices.

NEW YORK UNIVERSITY
New York, New York 10003

291. ENERGY-RELATED ATOMIC AND MOLECULAR STRUCTURE AND SCATTERING STUDIES $73,000 01-03
Benjamin Bederson
Department of Physics

A program is underway to study energy-related parameters of highly polar molecules and atomic systems such as O, N, C, and S. During the past year we have been concentrating on the first stage of this program, which is to measure the electric dipole polarizabilities of alkali halide dimers such as CsCl, RbCl, and NaCl. We are now performing similar measurements on the monomers (because of the presence of permanent electric dipole moments, no measurements of these important parameters exist). At the same time we have completed construction of an entirely new beams apparatus, designed for the study of collisions between electrons and atoms and simple molecules, with hiterto unattainable energy and angular resolution, using polarized beams in ground and excited states.

UNIVERSITY OF NEW MEXICO
Albuquerque, New Mexico 87131

292. ATOMIC PHYSICS WITH RELATIVISTIC BEAMS $80,000 01-03
H. C. Bryant
Department of Physics and Astronomy

A relativistic beam of ions at the Clinton P. Anderson Meson Physics Facility at Los Alamos (LAMPF) offers a unique opportunity to study fundamental processes in basic atomic systems. Using the 800 MeV ($\beta = .842$) H^- beam at LAMPF and a quadrupled Nd:YAG laser, photon energies, continuously tunable in the range from 0.35eV to 16eV by changing the angle between the two beams, can be produced in the barycentric system of the H^- ion. This technique enables us to study the single photon excitation of vacuum UV resonances in the H^- system and states in the H°. We are especially interested in the effects of strong electric fields (several MV/cm) produced by the relativistic transformation of laboratory magnetic fields. We are measuring the cross sections for single and double electron photodetachment from H^- in the photon energy range from 0.50eV to 16eV. The production of very high Rydberg states in H° which dissociate in the motional electric fields produced by weak magnetic fields in the laboratory is seen to play an important role in the two-electron cross section near threshold.

COLLEGE OF WILLIAM & MARY
Williamsburg, Virginia 23185

293. THE MEASUREMENT OF ABSOLUTE DETACHMENT CROSS SECTIONS OR NEGATIVE IONS FOR ENERGIES NEAR THRESHOLD $43,400 01-03
R. L. Champion and L. D. Doverspike
Department of Physics

The objective of this project is to measure various reactions which occur for gas phase collisions of negative ions with atoms and molecules, thus providing basic information essential to understanding the chemical pathways of negative ions in a variety of environments. The energy range of the experiments is typically from threshold for electron detachment of the negative ion up to several hundred electron-volts. Both absolute total and relative doubly-differential cross sections are measured. The reactants studied thus far include halogen negative ions, H^-, D^- and O^- in collisions with the inert gases and various molecular targets. The processes investigated include collisional detachment, elastic and inelastic scattering, reactive (ion-molecule) scattering, and collision-induced-dissociation. The combination of total and differential cross section measurements provides detailed information which, in turn, is used to test proposed collisional models, theories, and calculations of potential surfaces.

UNIVERSITY OF KANSAS
Lawrence, Kansas 66045

294. MANY-BODY PROCESSES IN ATOMIC AND MOLECULAR PHYSICS $34,780 01-03
Shih-I Chu
Department of Chemistry

The fundamental goals of this project are to develop nonperturbative quasienergy methods for investigating atomic and molecular processes in intense fields. (1) A semiclassical theory of multiphoton enhancement of vibrational excitations by molecular collisions is being developed. The vibrational-field surfaces which exhibit avoided-crossings are determined via Floquet theory. Transition among the dressed quasienergies are studied using the semiclassical time-dependent theory. (2) A practical method for calculating resonance energies and widths(lifetimes) of metastable states of van der Waals molecules, incorporating the use of complex coordinate transformation and square-integrable basis functions, is being developed. Besides involving only bound-state calculations and being free from boundary conditions, the method can be readily extendable to multichannel coupling problems.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

295. STORED-ION COLLISION MEASUREMENTS $47,000 01-03
D. A. Church
Department of Physics

Techniques to measure reaction rates and cross-section of multi-charged ion collision processes with atoms, molecules, photons, and electrons are being developed and implemented. Multi-charged ions at near-thermal energies are produced and confined in quadrupole structures using magnetic and electric fields. Resonant excitation and detection methods are employed to measure, characterize, and control the ion number, type, and mean energy distribution. Emphasis is currently placed on typical contaminants of fusion plasmas: e.g. ions of C, N, and O; and their charge-capture reactions with H atoms. The detection of de-excitation radiation following reaction is planned. Results of certain measurements can be compared with theoretical calculations.

UNIVERSITY OF TOLEDO
Toledo, Ohio 43606

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

A program of semi-empirical studies is being carried out with the goal of reliably predicting properties of large classes of atomic systems from existing data together with a few crucial new measurements. The high precision requirements in spectroscopic term analyses often exceed the existing capabilities for ab initio theoretical calculations, but the high degree of regularity among similar atomic systems can permit extremely accurate semi-empirical formulations. Existing semi-empirical methods are being extended to include the much heavier and more highly ionized systems which often occur in controlled fusion devices, and analogous semi-empirical approaches are being developed for the study of lifetimes and transition probabilities. These studies have provided some interesting predictions concerning the behavior of a number of specific systems, which might have gone unnoticed in a less intuitive approach.

HARVARD COLLEGE OBSERVATORY
Cambridge, Massachusetts 02138

297. THEORETICAL STUDIES OF HIGHLY IONIZED SPECIES A. Dalgarno and G. A. Victor Center for Astrophysics	$94,000	01-03

It has been shown that charge transfer recombination and charge transfer ionization are important processes in determining the degree of ionization in partly neutral plasmas and in plasmas modified by the injection of neutral particles. Detailed calculations are continuing on the efficiencies of charge transfer recombination for several different ionic systems and the results applied to the estimation of the ionization balance in different physical environments. Several other processes which may affect the behavior of ionized species in gas mixtures are under study by theoretical methods. The applicability of the various processes as diagnostic probes of the physical environment of the plasmas is being explored.

UNIVERSITY OF CHICAGO
Chicago, Illinois 60637

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

The goal of this project is to identify mechanisms that control the correlated motion of particles in collisions and in photoprocesses and to evaluate their effects. Two characteristic modes of electron motion along potential ridges have been identified this year, which should control the probability of excitation to different levels. Current efforts are directed to determine the resulting probabilities. Many aspects of the Stark effect of Rydberg levels have been sorted out and a new analytical formula has been constructed for the phaseshift of escaping electrons. It has been discovered by theory that the photodetachment of H^- leaving the residual H atom excited leads to ejection of photoelectrons in directions orthogonal to rather than parallel to the light polarization, even though this process is parity favored. This phenomenon reflects unexpected aspects of electron correlations within the excited H^- ion.

VANDERBILT UNIVERSITY
Nashville, Tennessee 37235

299. THEORETICAL STUDIES OF ATOMIC TRANSITIONS $58,000 01-03
Charlotte Froese Fischer
Computer Science Department

Atomic transitions are mechanisms for energy transfer in atomic sytems. A knowledge of the transition energy and the transition probability (or f-value) is often of fundamental importance as, for example, in fusion research. The present research is part of an ongoing project in atomic structure calculation using the MCHF method. Several transitions involving excited states have been studied including an analysis of the f-value trend along an isoelectronic sequence in the presence of level crossing and transitions to the Rydberg ^1D series in Ca I. In order to gain some insight into important cascade corrections to the experimental beam-foil data for the Al I sequence where some large discrepancies exist between theory and experiment, the lifetimes of several low-lying states were determined. Finally, the source of a 1.2% discrepancy between a previous theoretical f-value for the resonance transition of sodium and a recently announced, highly accurate experimental f-value will be investigated.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

300. FREE CHARGED PARTICLE BEHAVIOR IN INTENSE LASER FIELDS — $29,000 — 01-03
24 mos.
FY80-81
David M. Fradkin
Department of Physics

The objective of this project is to perform a theoretical analysis of the effects that intense laser pulses, with and without auxiliary electromagnetic field configurations, have on the dynamics of free charged particles. This study of free charged particle-radiation interactions is designed to provide insight into the mechanisms of energy transfer, the use of the laser as a particle accelerator, the effects that are produced by intense fields, and processes that take place in the astrophysical realm. Classical as well as quantum-mechanical treatments of models of the interaction between particles and fields are being investigated, with particular attention focussed on the amount of momentum-energy transfer to the charged particle. The influence of radiation reaction, laser polarization, special auxiliary field configurations, and the nature of asymptotic spin direction change, magnetic moment behavior, and other aspects, are also being investigated.

SRI INTERNATIONAL
Menlo Park, California 94063

301. STUDIES OF AUTOIONIZING STATES RELEVANT TO DIELECTRONIC RECOMBINATION — $57,100 — 01-03
T. F. Gallagher
Molecular Physics Department

The goal of this work is to reach an understanding of autoionization of atoms with two valence electrons and how it is affected by external perturbations such as electric fields. To do this, a powerful technique has been developed in which alkaline earth atoms in a low density atomic beam are excited by the successive absorption of three dye laser photons to specific autoionizing states, the decay of which produces ions and electrons which are detected. Total autoionization rates are obtained from the observed linewidth of the exciting transition, and the final states of the resulting ion and electron are determined from the energy analysis and angular distribution of the ejected electrons. The effects of an electric field on the autoionization rate is easily studied by applying a dc field. Thus it is possible to extract intrinsic and perturbed autoionization rates.

UNIVERSITY OF OKLAHOMA
Norman, Oklahoma 73019

302. EXPERIMENTAL AND THEORETICAL STUDY OF VERY LOW INELASTIC PROCESSES IN ELECTRON-MOLECULAR COLLISIONS $72,000 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 ($e-CO_2$). This work seeks to resolve numerous significant discrepancies between various determinations of near-threshold electron-impact excitations of molecules ($e-H_2$) 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 $e-H_2$ scattering, but in the future e-N2, e-CO, and $e-CO_2$ scattering will be considered.

LOUISIANA STATE UNIVERSITY
Baton Rouge, Louisiana 70803

303. ELECTRON COLLISIONS WITH POSITIVE IONS $47,200 01-03
Ronald J. W. Henry
Department of Physics and Astronomy

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 for excitation to approximately 4 times the ionization energy. Calculations are based on a close coupling expansion which includes the important physical effects of electron exchange and resonances. The lithium-like ion O^{5+} is the test case chosen for the theoretical methods under development. Studies of Fe^{23+} and other Cr, Fe, Ni, and Ti ions will be made. Methods for extrapolation along isoelectronic sequences are being investigated.

OREGON STATE UNIVERISTY
Corvallis, Oregon 97331

304. THERMAL-ENERGY SCATTERING OF ATOMS IN HIGH RYDBERG STATES $39,000 01-03
C. 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. The cross sections are virtually independent of the principal quantum number. Since ion-beam scattering experiments have heretofore proven difficult at thermal energies, this research program seeks to develop and exploit a useful new method for the determination of velocity-resolved free-ion differential cross sections and the functional form of ion-atom and ion-molecule interaction potentials.

SMITHSONIAN ASTROPHYSICAL OBSERVATORY
Cambridge, Massachusetts 02138

305. MEASUREMENTS OF IONIZATION BALANCE PARAMETERS IN ATOMIC IONS $75,000 01-03
John L. Kohl

The objective of this program is to provide measurements of those atomic parameters which govern the charge state distribution of atomic ions in high-temperature plasmas. The initial quantity to be measured is the energy integrated absolute cross section for dielectronic recombination in C^{+3} involving the 2s-2p stabilizing transition. The measurements test basic theoretical formulations of the dielectronic recombination process. The experimental approach uses coincidence techniques to measure two products (photon and C^{+2} ion) of dielectronic recombination events which occur at the intersection of a C^{+3} ion beam and an inclined electron beam. The coincidence technique discriminates and discards photons and C^{+2} ions which are formed individually by processes other than the specific dielectronic recombination process of interest. The first step in this program, initiated in May 1980, is to assemble the apparatus and to detect photon-ion coincidences which indicate the occurrence of individual dielectronic recombination events.

UNIVERSITY OF ARKANSAS
Fayetteville, Arkansas 72701

306. A THEORETICAL STUDY OF ELECTRON CAPTURE IN ION-ION AND ION-ATOM COLLISIONS $32,200 01-03
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.

KANSAS STATE UNIVERSITY
Manhattan, Kansas 66506

307. ATOMIC PHYSICS OF STRONGLY CORRELATED ELECTRONS $54,000 01-03
Chii-Dong Lin
Department of Physics

The goals of this project are to develop new theoretical methods for studying atomic excitations by the impact of photons, electrons and heavy particles. These fundamental processes are important in determining the physical properties of various ionized gases under astrophysical and laboratory conditions. In the area of photon and electron impact, a new method is being developed by treating the particles together as a point moving in a hyperspherical space under the influence of a multi-dimensional potential. The basic mathematical properties of the electronic wave functions are studied for the two-electron systems in this new and unconventional approach. In the context of heavy ion-atom collisions, the role of charge transfer as a mechanism of removing inner-shell electrons is shown to be predominant for near-symmetric collisions.

U. S. NATIONAL BUREAU OF STANDARDS
Boulder, Colorado 80309

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

This program is directed toward making fundamental advances in our knowledge of, and ability to calculate both accurately and efficiently, cross sections for collision processes involving electrons and atoms, ions and molecules. High precision calculations of elastic scattering of electrons by helium atoms, in the energy range used for absolute calibration of measurements for many atoms and molecules, are nearing completion. The effect of near-threshold resonances in electron impact excitation of helium-like ions is being investigated. A significant improvement in the computational software needed to include effects of exchange in electron-molecule collisions has been completed, and detailed calculations for several polar molecules ($HC\ell$, HF, KOH) are underway.

KANSAS STATE UNIVERSITY
Manhattan, Kansas 66506

309. ATOMIC PHYSICS WITH HIGHLY IONIZED IONS $400,000 01-03
P. Richard
Department of Physics

The fundamental goals of this program are to understand the electron transfer processes in systems with highly charged ions, the single and multiple inner-shell vacancy processes of excitation and ionization with heavy ions, and the deexcitation rates of few electron ions. A new method of studying electron capture by highly charged ions at very low velocity (e.g., $\sim$ 100 eV/amu 8^+ Ne) is being implemented by using the recoil ions from MeV/amu heavy-ion beams. Target K-shell to projectile K- and L-shell transfer and double K-shell to K-shell transfer are being studied by total cross section measurements. In addition, the impact parameter dependence of K-shell to K-shell charge transfer is being studied in nearly symmetric collisions as a test of the reaction mechanism. A second Born calculation for charge transfer is being developed. Ionization of one electron ions by H and He are also being investigated as a stringent test of ionization theories. The cross sections for radiative electron capture to the K-shell by zero- and one-electron ions in He are being measured. Calculations of multiplet factors, transition rates, multiplet partial fluorescence yields are performed.

Atomic Physics, continued

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

310. PHOTOIONIZATION OF ATOMS James A. R. Samson and A. F. Starace Department of Physics	$40,000	01-03

The main aim of this experimental and theoretical project is to unravel the effects of electron correlation and spin-orbit interaction on atomic photoionization processes. Photoionization cross sections of open shell atoms, such as O and Cℓ, are being measured. In addition, the angular distribution of photoelectrons from Cs is being studied. A new random phase approximation for the calculation of open and closed shell photoionization cross sections is being developed. The Rydberg energy spectrum and oscillator strengths of atomic hydrogen are being calculated for magnetic fields of order 10^5 Gauss using a basis of oblate spheroidal angle functions.

UNIVERSITY OF NORTH CAROLINA
Chapel Hill, North Carolina 27514

311. EXPERIMENTAL STUDIES OF ATOMIC INNER SHELL IONIZATION PHENOMENA Stephen Shafroth Department of Physics	$49,900 15 mo. FY79-80	01-03

The study of inner shell ionization phenomena is important both from a basic as well as an applied science point of view. The signature of an inner shell ionization process is a characteristic x-ray or an Auger electron. X-rays are detected with Bragg spectrometers and semiconductor detectors. Electrons are detected with a 30° parallel plate spectrometer. Systematic studies of x-ray and Auger processes require the capability of accelerating a wide variety of projectiles. This is now possible at TUNL by using the newly installed sputter ion source. Important inner shell ionization phenomena which are being studied are: double K vacancy production and radiative electron capture in fast projectiles. A program is underway to measure dielectronic recombination cross sections. This process is important for magnetically confined fusion power generators, since it is an energy loss process in Tokamaks.

UNIVERSITY OF COLORADO
Boulder, Colorado 80309

312. NEAR RESONANT ABSORPTION BY ATOMS IN INTENSE, FLUCTUATING LASER FIELDS — $60,000 — 01-03
Stephen J. Smith
Joint Institute for Laboratory Astrophysics

The goal of this project is to provide well-characterized quantitative data for the influence of field fluctuations on near-resonant absorption by atoms in intense laser fields. The absorption characteristics obtained using a carefully stabilized, very intense continuous wave laser field are compared with the characteristics when statistically well-characterized fluctuations are imposed on the same laser beam, using acousto-optic and electro-optic modulating devices. Techniques are being developed to impose phase fluctuations and amplitude fluctuations, to obtain data in forms appropriate to test various theoretical models. Measurements are carried out using a beam of atomic sodium in high vacuum, optically pumped to a specific substate so the absorbing $3S_{1/2} \rightarrow 3P_{3/2}$ transition is completely defined, and Doppler effects are reduced. A specially developed cw ring laser, with a line width of <100 kHz obtained by advanced stabilization techniques provides the intense field. Absorption is studied by observing fluorescence and also by using an additional laser as a probe to excite $3P_{3/2}$-4D transitions.

UNIVERSITY OF TENNESSEE
Knoxville, Tennessee 37916

313. DIFFERENTIAL CHARGE TRANSFER TO THE CONTINUUM BY IONS IN ATOMIC HYDROGEN — $42,000 — 01-03
Robert S. Thoe and Ivan A. Sellin
Department of Physics

Studies of electron capture to continuum states for bare ions moving through gaseous targets will be extended to the case of an atomic hydrogen target. In particular the doubly differential cross section for the case of protons, oxygen, and carbon nuclei incident on atomic hydrogen will be measured, and compared to recent second Born calculations. Such measurements require the development of an atomic hydrogen target suitable for use with an electron spectrometer.

WRIGHT STATE UNIVERSITY
Dayton, Ohio 45431

314. DYNAMICS AND THRESHOLD BEHAVIOR OF ENDOTHERMIC NEGATIVE ION-NEUTRAL RECTIONS

$78,000 01-03

Thomas O. Tiernan and Richard L.C. Wu
Brehm Laboratory and Department of Chemistry

The objectives of this project are to investigate the dynamics and threshold behavior of selected negative ion-neutral collision processes in the translational energy regime below 150eV (LAB). Excitation functions and energy thresholds are being determined for endothermic collision-induced dissociation and charge transfer reactions of FeO^-, FeO_2^-, PO^-, PO_2^-, and AlO_2^- using a tandem mass spectrometer. These measurements provide thermochemical data for the ionic species including bond dissociation energies and heats of formation, as well as electron affinities for the corresponding neutral molecules. The kinematics of some of these endothermic reactions are also being determined using a crossed ion-molecular beam apparatus, in which the angular and translational energy distributions of the products are measured. These data yield insight into the microscopic mechanisms of endothermic ion-neutral reactions.

RICE UNIVERSITY
Houston, Texas 77001

315. ENERGETICS OF ATOMIC AND MOLECULAR INTERACTIONS

$215,000 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, as well as interactions at solid surfaces. Research areas include reactions and radiative lifetimes in atomic and molecular systems of high-efficiency laser promise, new approaches to the study of solid surfaces, 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 and quenching rates for excimer laser transitions. Spin polarization effects in low energy electron diffraction (LEED) show promise as the basis for an improved surface diagnostic method. New theoretical results include reliable cross sections for excitation and charge transfer in H^+-$He^+(n\ell)$ collisions over the energy range .6-15 kev. Also the sensitivity to plasma characteristics of hydrogenic ion production by electron impact in a dense hot plasma is under theoretical study.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

316. X-RAY EMISSION IN HEAVY-ION COLLISIONS $50,000 01-03
R. L. Watson
Cyclotron Institute and Department of Chemistry

The objectives of this project are to identify various environmental influences on x-ray emission from highly ionized atoms produced in high energy ion-atom collisions and to understand their behavior. Studies of x-ray emission from heavy-ion-excited target atoms have shown that the relative intensity distributions of Kα x-ray satellites are altered by the rapid transfer of electrons from the surroundings. These effects are observed by varying the chemical composition of the target and by comparing the spectra of solids and gases. In the case of x-ray emission from highly stripped projectile ions, the high density of electrons in a solid-state environment enables collisional excitation and decay processes to compete with x-ray and Auger decay. This situation leads to the observation of serious line broadening and to line shifts resulting from the "dynamic" screening of the projectile charge by the electrons of the medium.

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

317. DETERMINATION OF SELECTED ATOMIC DATA PERTINENT TO THE MFE PROGRAM $120,000 01-03
W. L. Wiese
Atomic and Plasma Radiation Division

This ongoing research program to determine selected atomic data has two major components: (a) Theoretical studies of atomic structures and processes and (b) The critical evaluation and compilation of atomic transition probability data. The atomic structure studies are concentrated on examining and assessing methods for attacking the correlation problem for systems which are also moderately affected by relativistic corrections. Currently, exploratory calculations are in progress on ions isoelectronic with first row atoms. Systematic survey calculations within the distorted wave approximation are being done for electron impact ionization cross sections of ions in the helium, lithium and neon isoelectronic sequences. The critical evaluation of transition probability data for atoms, in all stages of ionization, of the iron group elements is the main current focus of the data center, and this project is nearing completion.

YALE UNIVERSITY
New Haven, Connecticut 06520

318. STUDIES OF THE HYDROGENATION OF SMALL UNSATURATED MOLECULES USING ORGANOMETALLIC CLUSTER COMPOUNDS AS CATALYSTS $55,000 02-01
Richard D. Adams
Department of Chemistry

The activation of small unsaturated molecules by transition metal cluster complexes and the transfer of hydrogen atoms from the metal atoms to the substrates are processes required for the development of cluster compounds as catalysts. The reactions of transition metal hydride cluster compounds $H_2Os_3(CO)_{10}$ and $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ with small unsaturated molecules are being investigated. Determination of the modes of activation, the nature of the hydrogen transfer and the structure and bonding of the partially hydrogenated substrates to the polynuclear metal frameworks are our principal goals. The reactions are monitored spectroscopically by infrared and nuclear magnetic resonance techniques. The products are analyzed structurally by x-ray crystallographic methods.

UNIVERSITY OF NORTH CAROLINA
Chapel Hill, North Carolina 27514

319. THE HEATS OF FORMATION OF GAS PHASE ORGANOSULFUR MOLECULES, RADICALS AND IONS MEASURED BY PIPECO $50,000 02-01
Tomas Baer
Department of Chemistry

The heats of formation of sulfur containing fragments, ions, and molecules are measured by photoion-photoelectron coincidence spectroscopy. *Ab-initio* calculations are also used to determine structures of these species. Comparison of the structure and energies with the corresponding oxygen containing species is a useful technique for learning about the unique bonding and reactivity characteristics of sulfur containing species. These data are important because of the central role of sulfur in the pollution resulting from coal and oil combustion.

Chemical Energy, continued

WEBER STATE COLLEGE
Ogden, Utah 84408

320. THE ROLE OF THE HYDROGEN-DONOR SOLVENT IN COAL HYDROLIQUEFACTION — $30,000 — 15 mo. — FY79-80 — 02-01
Robert R. Beishline
Department of Chemistry

When coal is hydroliquified using tetralin (Tet) as a donor solvent, 1,2-dihydronaphthalene (1,2-DHN) is an intermediate in the dehydrogenation of Tet to naphthalene (Nap). The objective of this research is to determine the nature of the intrasolvent hydrogen transfer reactions in which 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 Tet and Nap have been measured (380-420°C) and the results are being analyzed to determine a mechanism that is consistent with the data. A method to quantitatively measure hydrogen is being set up, since several plausible mechanisms require the formation of H_2. Because the data suggest the presence of free radicals, the fate of Tet and 1,2-DHN in the presence of free radicals will be compared by pyrolyzing these compounds in the presence of tetraphenyl ethane which dissociates into diphenylmethyl radicals at appropriate temperatures (300-400°C).

TEXAS A&M UNIVERSITY
College Station, Texas 77843

321. THE APPLICATION OF FUNCTIONALIZED POLYMERS IN CATALYSIS — $34,000 — 02-01
D. E. Bergbreiter
Department of Chemistry

Specific objectives of our studies of applications of polymers in catalysis include: the synthesis of functionalized organic polymers which can trap reactive soluble intermediates from heterogeneous catalytic reactions; a study of the effect of organometallic reducing agents on polymer-bound titanium olefin hydrogenation and isomerization catalysts; and finally, the preparation and application of soft acid containing polymers to homogeneous catalytic systems to absorb free soft bases (triarylphosphine ligands) from solution to prepare <u>in situ</u> more reactive homogeneous catalysts. Overall, the goal of our project is to show the applicability and potential for readily functionalized polymers in studies of catalytic reactions.

STANFORD UNIVERSITY
Stanford, California 94305

322. CATALYTIC STEAM GASIFICATION OF CARBON Michel Boudart Department of Chemical Engineering	$83,844 18 mo. FY80-81	02-01

The fundamental goal of this project is to understand the mechanism of the platinum catalyzed gasification of carbon by water vapor and hydrogen. Kinetic studies under differential conditions are underway to determine reaction order, activation energy, product selectivity, effect of product inhibition and kinetic isotope effects. All Pt/carbon samples are evacuated at 1225K to remove adsorbed oxygen and hydrogen. The reactions are carried out between 833 and 1173K by flowing water vapor and hydrogen in a stream of helium through a packed bed of carbon containing platinum crystallites. Physical adsorption of nitrogen and hydrogen titration of preadsorbed oxygen are used to measure total and platinum surface areas. Results from the catalyzed carbon-hydrogen reaction have permitted significant progress in understanding the reaction mechanism. Hydrogen inhibition has been found to be important in limiting the overall rate of the catalyzed carbon-steam reaction.

WAYNE STATE UNIVERSITY
Detroit, Michigan 48202

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

A broad study is being conducted of a new class of catalysts: transition metal carbonyl complexes directly deposited on high surface area inorganic supports. These catalysts have the potential of combining some of the advantages of homogeneous catalysts (by virtue of the use of molecular precursors) with the high stability of traditional heterogeneous catalysts. The recently developed technique of temperature programmed decomposition (TPDE) is being used to efficiently characterize these materials during catalyst synthesis. Means of controlling the nature of the final catalyst, both with regard to its average carbonyl stoichiometry and oxidation state, are being investigated. In particular, carbonyls are being used as a route to supported low-valent metals which can not be prepared by traditional techniques of catalyst synthesis. Information from TPDE is being correlated with activity data to obtain a structure-activity relationship. Several catalysts which are 100-fold more active than their traditional analogues for methanation, hydrogenation, and hydrogenolysis are being studied in more detail.

Chemical Energy, continued

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

324. THE PROPERTIES OF SUPPORTED METAL CATALYSTS $90,000 02-01

R. L. Burwell, Jr. - Department of Chemistry
J. B. Butt - Department of Chemical Engineering
J. B. Cohen - Department of Materials Science & Engineering

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/SiO_2, Pt/Al_2O_3 and Pd/SiO_2 varying in percentage exposed of metal component from ca.10 - 90%. Extensive x-ray characterization has been carried out on Pt/SiO and is underway for Pt/Al_2O_3 and Pd/SiO_2. Chemisorption studies on the reactivity of the Pt or Pd surface with oxygen and hydrogen have been nearly completed. A major finding has been that the apparent structure sensitivity of probe reactions such as the hydrogenolysis of cyclopropane or methylcyclopropane and deuterium exchange with cyclopentane can be altered at will by the particular conditions of pretreatment in hydrogen prior to reaction. The study is now being extended to alloys, using Co-Rh.

UNIVERSITY OF WISCONSIN
Madison, Wisconsin 53706

325. MECHANISTIC STUDIES RELATED TO THE METAL CATALYZED HYDROGENATION OF CARBON MONOXIDE TO HYDROCARBONS $159,095 27 mo. FY80-81 02-01

Charles P. Casey
Department of Chemistry

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. The kinetic and thermodynamic stability of the metal formyl compounds are being determined. It is crucial to know the thermodynamic stability of M—CO—H relative to M—H + CO to assess whether metal formyl species (M—CO—H) are viable intermediates in CO reduction. Hydroxymethyl metal compounds (MCH_2OH) have also been prepared as intermediates in CO reduction. These compounds are being synthesized and their reactions with CO, H_2, acids, and bases are being studied. The synthesis and reactions of heterobimetallic compounds are being studied as potential new catalysts for CO reduction.

INDIANA UNIVERSITY
Bloomington, Indiana 47405

326. ACTIVATION AND CO-ACTIVATION OF MOLECULAR HYDROGEN AND CARBON MONOXIDE BY TRANSITION METAL AND MIXED METAL ALKOXIDES AND OXIDES $50,000 02-01
Malcolm H. Chisholm
Department of Chemistry

Fischer-Tropsch catalysts are mixed metal oxides and are used commercially for the conversion of syn-gas (CO + H_2), which is available from coal, to hydrocarbons (petrols and gasolines) and alcohols. We are making metal alkoxides, which are known to mimic metal oxide structures, and investigating their reactions with molecular hydrogen and carbon monoxide. We are also trying to make hydrido and carbonyl transition metal alkoxides by a variety of synthetic routes. We believe these compounds will provide models for giving an understanding of the heterogeneous Fischer-Tropsch Chemistry.

WESLEYAN UNIVERSITY
Middletown, Connecticut 06457

327. HOMOGENEOUS CARBON MONOXIDE FIXATION $50,000 02-01
Alan R. Cutler
Department of Chemistry

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 Cp 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.

ROCKWELL DIVISION/ATOMICS INTERNATIONAL
Canoga Park, California 91304

328. MOLTEN SALT INTERACTIONS IN COAL PROCESSING $150,000 02-01
G. B. Dunks
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 salts. Parametric studies of the oxidation of graphite in molten sodium carbonate, molten sodium sulfate and molten mixtures of the two salts using air or oxygen are employed to define the identity and quantity of the volatile products, the temperature dependence of the processes and the variation in the reaction rate with respect to oxygen and carbon dioxide concentration and the surface area of the graphite. Electrochemical methods are being employed to determine the identity and concentration of the ionic species in molten sodium carbonate with respect to variation of oxygen and carbon dioxide partial pressures. Subsequently, graphite will be added to the sodium carbonate melt and the resultant shifts in the concentrations of the melt components determined. The latter studies will be extended to include molten sodium sulfate and molten sodium carbonate-sodium sulfate mixtures.

UNIVERSITY OF TEXAS
Austin, Texas 78712

329. STUDY OF FISCHER-TROPSCH SYNTHESIS THROUGH THE USE OF SURFACE INTERMEDIATE SCAVENGERS $117,100 02-01
3 years
FY80-82
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. This includes: identification of the reaction intermediates, the means by which they react and the means by which they are influenced by the synthesis variables. The synthesis reaction is carried out over oxide supported Fe, Ru and Ni at pressures ranging from 1 to 10 atmospheres. Cyclohexene is added to the feed gas, H_2 and CO, and reacts with C_yH_x intermediates, alkyl and/or alkylidene, to generate alkyl substituted cyclohexenes and cyclohexanes. The distribution of substituted cyclic products is representative of the distribution of C_yH_x intermediates. Scavenged product dependence on synthesis conditions and catalyst composition will be used to develop reaction mechanisms, kinetic expressions and an understanding of synthesis selectivity.

UNIVERSITY OF VERMONT
Burlington, Vermont 05401

330. CHEMICALLY MODIFIED CARBON, PLATINUM AND NICKEL ELECTRODES — $51,729 — 02-01
C. M. Elliott
Department of Chemistry

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

331. SYNTHESIS, CHEMISTRY AND CATALYTIC ACTIVITY OF COMPLEXES OF LANTHANIDE AND ACTINIDE METALS IN UNUSUAL OXIDATION STATE AND COORDINATION ENVIRONMENTS — $57,000 — 02-01
William J. Evans
Department of Chemistry

The objective of this investigation is to identify the special chemical properties of the lanthanide metals 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 metathesis, hydrogenolysis, and thermal decomposition reactions of $(t\text{-}C_4H_9)_4LnLi$ and $(C_5H_5)_2Ln$-alkyl complexes. The former complexes are interesting because they are the only tert-butyl organometallics which do not decompose via the common β-hydride elimination pathway. New organolanthanide complexes involving allenyl and hydride ligands are being synthesized to model the catalytically active lanthanide complexes recently discovered by vaporizing lanthanide metal atoms into an alkyne matrix. Electrochemical and photochemical studies of organolanthanides are also in progress to further establish the unusual features of the chemistry of these elements.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

332. HOMOGENEOUS CATALYSIS OF THE WATER GAS SHIFT REACTION $99,519 02-01
18 mo.
FY79-80
Peter C. Ford
Department of Chemistry

The objective of this study is to understand the fundamental chemical mechanisms related to the solution phase catalysis of the water gas shift reaction by metal carbonyl complexes. Major attention is being directed toward two systems based on ruthenium carbonyl. In alkaline solution, the catalytic cycles are apparently dominated by ruthenium hydride carbonyl clusters, but a different behavior is seen in acidic solution where mononuclear ruthenium carbonyl complexes are predominant. The tools employed in these investigations include both reaction kinetics and <u>in situ</u> spectral characterization of catalyst components. Elucidation of the catalysis mechanisms will provide the basic information for the design of new, more active catalysts for this reaction important to the production of synthetic hydrocarbon fuels.

CORNELL UNIVERSITY
Ithaca, New York 14853

333. ESR STUDIES OF SURFACE ADSORPTION AND CATALYSIS UNDER ULTRA-HIGH VACUUM CONDITIONS $65,000 02-01
Jack H. Freed
Department of Chemistry

The objective of this project is to develop 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 experimental design utilized in this project, the microwave cavity is itself part of the UHV system so that clean metallic surfaces may be prepared by vacuum evaporation onto the interior of the cavity walls. Various clean gases may then be directly adsorbed onto the surface and <u>in situ</u> ESR spectra may be obtained to study paramagnetic adsorbates and surface reaction kinetics. Then, by studying these clean surfaces with established UHV techniques, it will become possible to directly interrelate the findings of the ESR experiments with those from these other methods.

Chemical Energy, continued

INDIANA UNIVERSITY
Bloomington, Indiana 47405

334. RADICAL CHAIN AND REARRANGEMENT REACTIONS IN COAL LIQUEFACTION — $50,000 — 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 CO_2 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 dipolymerizing 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

335. MECHANISTIC STUDIES OF CARBON MONOXIDE REDUCTION — $40,000 — 02-01
Gregory L. Geoffroy
Department of Chemistry

Transition metal cluster compounds are being employed as models to probe the mechanisms by which metal surfaces catalyze the reduction of CO by H_2 to produce methanol and hydrocarbons. Reasonable mechanistic schemes for the surface catalyzed reactions have been proposed and the likelihood of the various intermediates in the individual reaction steps are being tested by examining the reactivity of appropriately selected or designed metal clusters. In a separate aspect of this study, mixed-metal dimers which should function as *homogeneous* catalysts for the reduction of CO are being designed and synthesized. Focus is on dimers involving combinations of early and late transition metals and metal-metal dimers involving the actinide elements.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

336. THE PREPARATION AND CHARACTERIZATION OF LIGAND TYPES INTERMEDIATE IN THE METAL-CATALYZED CONVERSION OF COAL TO METHANE, METHANOL, AND HIGHER ALKANES AND ALCOHOLS — $78,000 — 18 mo. — FY79-80 — 02-01
John A. Gladysz
Department of Chemistry

The preparation of homogeneous complexes containing ligand types believed to be intermediate in the metal-catalyzed conversion of carbon monoxide to organic molecules (methane, methanol, gasoline) is being attempted. 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 ($-CH_3$) and carbonyl ($-CO$) complexes are produced. The stabilization of hydroxyalkyl complexes by chelation is being attempted. Carbonylation studies of these various ligand types are being carried out in order to determine possible modes of carbon chain growth under Fischer-Tropsch reaction conditions.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

337. CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDIES OF HYDROCARBONS — $132,000 — 18 mos. — FY79-80 — 02-01
David M. Grant and Ronald J. Pugmire
Departments of Chemistry
and Fuels Engineering

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.

Chemical Energy, continued

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91125

338. 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

The objectives of the research are to understand the fundamental mechanisms of hydrocarbon reactions and to develop new methods for the reduction of carbon monoxide to useful organic products. Transition metal alkyl complexes are being studied as models for intermediates in hydrocarbon reactions. Those reactions resulting in C-C bond cleavage are of particular interest. A new method of reducing carbon monoxide to formaldehyde and methanol has been discovered. Attempts are now under way to develop this reaction to give higher yields of these products in a catalytic reaction.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

339. METALLOCARBORANCES STRUCTURALLY ENGINEERED FOR THE REDUCTION OF CARBON MONOXIDE M. Frederick Hawthorne Department of Chemistry	\$110,000 24 months FY80-81	02-01

The currently accepted hypothesis that the reduction of carbon monoxide to hydrocarbons requires the cooperativity of two or more metals is being investigated by the synthesis of a variety of polymetallocarborane clusters of various configurations in which the metals are held in essentially rigid positions with respect to one another. The interaction of carbon monoxide with these complexes is being explored. Characterization by usual methods will be supplemented with X-ray structural determinations as warranted. The kinetic stability of metallocarborane clusters in general lends them considerable potential as catalysts even under somewhat forcing conditions. The potential of the various carbonyl complexes as homogeneous methanation catalysts will be determined over a range of temperatures and pressures to optimize catalytic activity.

RUTGERS UNIVERSITY
Newark, New Jersey 07102

340. STUDY OF ION PAIR DIMERIZATION IN LOW DIELECTRIC SOLVENTS — $42,000 — 02-01
16 mo.
FY79-80
Paul R. Hemmes
Department of Chemistry

The basic objective of this work is to improve the electrical conductivity of solutions of lithium salts in ether-like solvents. This is done by hindering the formation of ion pairs and ion pair dimers. A kinetic approach to this has been adopted using an electric field modulation kinetic spectrometer which directly measures the relaxation time of the conductance. The concentration dependence of the relaxation time allows us to estimate the ion pair dimer formation constant. It has been found that dimers exist in both solvent separated and contact forms. The formation of dimers (and ion pairs themselves) can be greatly reduced by adding complexing agents. Cation complexing agents lead to poor electrochemical behavior of lithium ion. A unique new class of anion solvating agents has been discovered which significantly improve the conductivity of certain lithium salts.

UNIVERSITY OF PITTSBURGH
Pittsburgh, Pennsylvania 15260

341. STUDIES OF SUPPORTED METAL CATALYSTS — $67,500 — 02-01
David M. Hercules
Department of Chemistry

The goal of this study is to characterize surface species of a calcined catalyst, to understand how they influence catalyst behavior. Surface spectroscopic techniques (ESCA, AES, SIMS, ISS, Raman, FTIR) were coupled with chemical treatment. Four species were found on Mo/Al_2O_3 catalysts: Mo in tetrahedral sites (Mo-t), Mo in octahedral sites (Mo-o), $Al_2(MoO_4)_3$ and MoO_3. Mo-t and Mo-o dominated below monolayer composition (20% MoO_3); bulk chemical phases appeared above monolayer composition. Conditions of catalyst treatment influenced Mo species. Co/Al_2O_3 catalysts showed Co-t, Co-o and bulk Co_3O_4. Co-t was inert to H_2 reduction (500°C); Co-o and Co_3O_4 were active. $Co/Mo/Al_2O_3$ is under study to determine the interaction between of Co and Mo. $Co/Mo/Al_2O_3$ has been studied with a laser microprobe mass analyzer (LAMMA) to investigate polymolybdate species. Nickel catalysts have been prepared with a variety of supports (Al_2O_3, SiO_2, TiO_2) and preparation techniques (impregnation, coprecipitation). The nickel species are influenced by the support and the method of preparation.

SRI INTERNATIONAL
Menlo Park, California 94025

342. HIGH TEMPERATURE CHEMISTRY OF HYDROGEN PRODUCTION CYCLES — $56,000 — 18 mo. — FY79-80 — 02-01
D. L. Hildenbrand
Materials Research Laboratory

This program is concerned with mechanistic studies leading to a better understanding of the thermodynamics and kinetics of metal sulfate decomposition and vaporization processes. These processes are being studied by the torsion-effusion method and by mass spectrometry, so that total pressure and vapor composition can be determined unambiguously, and equilibrium thermodynamic data can be derived. Departures from equilibrium due to kinetic barriers are treated by a semitheoretical model. Currently being studied are the sulfates of zinc, copper, iron and sodium. Of particular interest are the catalytic effects of certain metal and oxide additives on the decomposition rates of sulfates evolving gaseous SO_3 rather than the dominant equilibrium species SO_2. To aid in understanding the latter, the catalytic reduction of SO_3 is being studied over a range of temperature using some of the additives found to be effective catalysts for metal sulfate decomposition.

UNIVERSITY OF DELAWARE
Newark, Delaware 19711

343. AUGER AND REACTION STUDIES OF POISONING BY SULFUR AND REGENERATION OF METAL SYNTHESIS GAS CATALYSTS — $200,000 — 24 mo. — FY80-81 — 02-01
J. R. Katzer and H. Windawi
Department of Chemical Enginering

The objectives of this project are to further develop our understanding of the sulfur tolerance of supported metal catalysts employed in the hydrogenation of CO, the effect of metal-support interaction on the sulfur tolerance, and the regenerability of these catalysts. Ni catalysts supported on TiO_2, ZrO_2, Ce_2O_3, as well as on Al_2O_3 are prepared and characterized. Their activities, selectivities, and sulfur tolerances are being investigated in both plug flow (differential mode) and stirred tank reactors. FTIR studies of functioning catalysts are being carried out and CO stretching frequencies are investigated both in intensity as well as shift and are correlated with catalyst activities. Studies of the deactivation of Ni and Co catalysts by sulfur in CO hydrogenation showed that Co catalysts unlike Ni show the accumulation of large quantities of surface carbon and undergo carburization which reduce the catalytic activity by a large amount. For Ni, sulfur poisoning occurs exclusively by surface blockage; for Co, sulfur and carbon poisoning appear to involve both geometric and electronic effects. The interrelationship between sulfur and carbon appears to be important and requires clarification.

NORTHWESTERN UNIVERSITY
Evanston, Illinois 60201

344. SOLID STATE, SURFACE AND CATALYTIC PROPERTIES OF OXIDES — $120,000 — 02-01
H. H. Kung — 24 mo.
Department of Chemical Engineering — FY80-81

The goal of this research is to seek fundamental understandings in oxide catalysis. Two research programs are being undertaken. In the first program, the selective oxidation of butene to butadiene on iron containing oxide is examined. Results to date indicate that the selective oxidation to butadiene and the total combustion to carbon dioxide take place on two separate sites. It is proposed here to elucidate the nature of these two oxidation sites by studying the reaction on well ordered iron oxide single crystal surfaces. The known atomic arrangements on these surfaces permit identification of the atomic environments of the sites. The role of chromium addition to iron oxide will also be examined. Experimental determination of the degree of surface segregation of chromium in a solid solution with iron oxide will be made. Theoretical calculations will be performed to aid the interpretation. The second program involves the elucidation of the nature of the active site for the decomposition of methanol on a zinc oxide single crystal surface.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

345. A STUDY OF CATALYSTS AND MECHANISMS IN SYNTHESIS REACTIONS — $104,214 — 02-01
Jack H. Lunsford — 24 mo.
Department of Chemistry — FY79-80

This research program is devoted to two aspects of synthesis reactions involving carbon monoxide and either hydrogen or water. One objective is to determine the catalytic properties of small metal particles, either in zeolites or on other supports, and the other is to explore the importance of gas phase radicals which are formed on catalytic surfaces. The selectivity of small metal particles may be remarkably dependent upon the type of support. For example, the reaction of carbon monoxide with hydrogen over palladium yields almost exclusively methane or methanol, depending on whether a neutral or an acid silica gel support is used. Moreover, the selectivity of the reaction between carbon monoxide and water to form methane is altered significantly when rhodium is supported on different materials. Gas phase π-allyl radicals are formed when propylene reacts with bismuth oxide. The radicals are trapped downstream from the catalysts, using a matrix isolation technique. When oxygen is also present, the corresponding peroxy radicals are formed.

DREXEL UNIVERSITY
Philadelphia, Pennsylvania 19104

346. PHYSICAL AND CHEMICAL STUDIES OF CHLOROPHYLL IN MICROEMULSIONS — $36,000 — 02-01
Raymond A. Mackay
Department of Chemistry

The goal of this project is to provide fundamental information on the nature of photoreactions in microemulsions and the utility of these media as solvents for solar energy absorbers. The photoreduction of adsorbed dye (principally methyl red) by ascorbate is being used as a test system. The effectiveness of chlorophyll a, other chlorins and various synthetic porphyrin sensitizers is evaluated by measurement of the quantum yield of the reaction. The operative mechanism is being explored by means of the reaction kinetics and stoichiometry. Other model systems involving reversible redox reaction partners are being sought. Detailed mechanistic studies will be undertaken with the completion of a flash photolysis apparatus.

STANFORD UNIVERSITY
Stanford, California 94035

347. MOLECULAR BEAM STUDIES OF THE DYNAMICS OF ACTIVATED ADSORPTION AND HETEROGENEOUS KINETICS ON SINGLE CRYSTAL SURFACES — $80,000, 16 mo., FY79-80 — 02-01
Robert J. Madix
Department of Chemical Engineering

The basic objective of this research is the understanding of reactive collisions between molecules from the gas phase with solid surfaces and between molecular species adsorbed on the surface. A molecular beam apparatus is being used which permits the measurement of the probability of reactions occurring with each molecular collision. The lifetimes of the reactants on the surface can be measured directly using pressure pulse techniques. Characteristic surface lifetimes between 10^{-1} and 10^{-5} are easily measured. Recent results indicate that the reaction of atomic oxygen with molecular hydrogen on single crystal surfaces of platinum proceeds via dissociative adsorption of the hydrogen prior to water formation. Studies are being performed to check the anomolous rate constant for H-atoms recombination on Pt(111) surfaces. The apparatus is also being modified to measure and control the dynamic variables in the collision in order to study the effects of incident translational energy and internal excitation on reactive collisions at the surface.

STANFORD UNIVERSITY
Stanford, California 94305

348\. ELECTROCATALYTIC OXIDATION OF GASEOUS HYDROCARBONS ON SOLID-OXIDE ELECTROLYTES — $53,000 — 02-01

David M. Mason
Department of Chemical Engineering

The primary goal of this study is to gain an understanding of the mechanisms of electro-catalytic processes occuring during the oxidation of hydrocarbons on solid oxygen-ion electrolyte anodes. Such information is necessary for the optimal design of solid electrolyte <u>fuel cells</u>. There is experimental evidence that F-centers and V-centers on the electrolyte act as active catalytic sites in reducing and oxidizing gaseous species at the cathode and anode respectively. The solid electrolyte: $(ZrO_2)_{0.98}(Sc_2O_3)_{0.2}$ at temperatures around 700°C-800°C is employed to study electro-oxidation of gaseous compounds derived from gasification of coal and wood such as: CO, H_2, CH_4, and CH_3OH or from fermentation such as: C_2H_5OH. A general survey of the electrochemical reactivity of the hydrocarbons shows the following trend: $H_2 > CH_3OH > CO > C_2H_5OH > CH_4$. More detailed studies are being made which focus on elucidating kinetic mechanisms by varying composition and temperature of the gaseous reactants as well as morphology of the electrode.

SRI INTERNATIONAL
Menlo Park, California 94025

349\. DETERMINATION OF FUNDAMENTAL THERMO-CHEMICAL AND KINETIC DATA FOR RADICAL SPECIES IMPORTANT IN COAL CONVERSION AND AROMATIC FUEL UTILIZATION — $77,474, 15 mo., FY80-81 — 02-01

D. F. McMillen and D. M. Golden
Department of Chemical Kinetics

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 radicals. This will help provide a basis for the reliable estimation of benzylic bond-cleavage rates for virtually any alkyl-aromatic structure in polycyclic aromatic systems, eliminating the need for actual laboratory measurements for each individual structure of importance in coals. Well documented correlations between resonance stabilization energy and the number of contributing Kekule structures in polycyclic aromatic hydrocarbons have recently been speculatively extended to benzylic radicals in the same polycyclic systems. The Very Low-Pressure Pyrolysis technique is being used to measure the rate of unimolecular decomposition of 9-ethylanthracene to give the 9-anthrylmethyl radical. These measurements are being extended to include also the 9-ethylphenenthrene system and the measurement of the rates of recombination of the corresponding benzylic radicals.

UNIVERSITY OF CALIFORNIA/SAN DIEGO
La Jolla, California 92093

350. HYDRIDE FORMATION H. Oesterreicher Department of Chemistry	$37,346	02-01

The purpose of this project is to gain a fuller understanding of various aspects in the phenomenology of hydride formation. In particular, parameters of interest include equilibrium pressures, heats of formation, amount of hydrogen uptake, kinetic as well as crystallographic and phase diagram data. Materials are chosen such that hydride formation takes place reversibly under conditions relatively close to ambient ones. For this purpose model calculations on the stability of hydrides are employed. Materials are further chosen so that a systematic understanding of factors involved in hydride formation such as size, valency or the influence of the nature of the metal hydrogen bond (ionic-covalent) will result. Typical systems of interest involve hydrides of Ca-Mg-Ni-B.

UNIVERSITY OF SOUTHERN CALIFORNIA
Los Angeles, California 90007

351. SUPERACID CATALYZED DEPOLYMERIZATION AND CONVERSION OF COALS George A. Olah Hydrocarbon Research Institute	$60,000	02-01

The superacid catalyzed depolymerization of coals, particularly of bitumenous Illinois #6, is studied under a variety of conditions. In model systems cleavage of methine, ethylidene, ether, sulfide, amino and other linkages is studied with various superacidic systems, particularly those which provide easy recovery and reuse of the catalytic superacids.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA
Santa Barbara, California 93106

352. REACTIONS OF METAL ATOMS AND CLUSTERS IN LOW TEMPERATURE MATRICES Ralph G. Pearson - Department of Chemistry Paul Barrett - Department of Physics	\$75,000 18 mo. FY79-80	02-01

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, Fe_2, and iron clusters and low temperature matrix isolated molecules of N_2, CO, HI, CH_4, and other small molecules are under investigation. A systematic study of the reactivity of palladium atoms and clusters with respect to simple organic molecules is also being carried out. The reactions of other transition metals that are of importance to catalysis will also be studied.

UNIVERSITY OF TEXAS
Austin, Texas 78712

353. CATALYTIC REDUCTIONS USING CARBON MONOXIDE R. Pettit Department of Chemistry	\$54,226	02-01

The object of the present work is to develop a series of complexes which will serve as catalysts for reductions using CO and H_2 simultaneously as the reducing agent. Such catalysts would thus allow direct utilization of synthesis gas for reductions instead of its further conversion to pure hydrogen. The same chemistry involved in the catalytic process envisioned above should also allow for the utilization of synthesis gas as the reductant in a fuel cell.

A series of metal carbonyls have been found to be active, in the presence of aqueous organic amines, as catalysts for the water gas shift reaction, i.e., the conversion of carbon monoxide and water to hydrogen and carbon dioxide. Catalytic turnover rates of 270,000 over a 10 hour period have been realized for $Ru(CO)_5$ and trimethylamine as a base.

PURDUE UNIVERSITY
Indianapolis, Indiana 46205

354. THE METAL-AMMONIA REDUCTION AND REDUCTIVE ALKYLATION OF COAL TAR HYDROCARBONS AND THE ^{13}C NMR CHARACTERIZATION AND CONFORMATIONAL ANALYSIS OF THE REDUCED PRODUCTS — $81,000 — 24 mo. — FY80-81 — 02-01
Peter W. Rabideau
Department of Chemistry

The solubility of aromatic compounds (including coal) in organic solvents is increased by reduction reactions due to one or more of the following processes: (1) reduction of the aromatic ring, (2) incorporation of alkyl groups (i.e., reductive alkylation reactions), and (3) carbon-carbon reductive bond cleavage. Hence, the fundamental chemistry of reduction processes by alkali metals in liquid ammonia is being investigated with relationship to these three points. Factors such as reaction conditions, structural types and substituents all play an important role, and the nature of the intermediate carbanions and radical/anions become a central issue. The conformational analysis of the reduced products is being investigated by ^{1}H and ^{13}C nuclear magnetic resonance, since geometric preferences in products often have significant effects on the course of these reductions.

MARQUETTE UNIVERSITY
Milwaukee, Wisconsin 53233

355. POLYMER-BASED CATALYSTS — $40,000 — 02-01
S. L. Regen
Department of Chemistry

The principal objective of this program is to develop efficient, stable and selective resin-based catalysts for accelerating aqueous phase-organic phase reactions. Current effort is being focused on ionic type polymers with the specific aim of understanding the relationship between macrostructure, microenvironment and catalyst activity. A large series of phosphonium-based polystyrene resins is being prepared having various cross-link densities, percent ring substitutions and porosities and is being evaluated for the triphase catalytic displacement by chloride ion on *n*-decyl methanesulfonate. Kinetic analysis is carried out by monitoring product mixtures using gas-liquid chromatography. Swelling measurements and ^{13}C nmr spectroscopy are being used to define the microenvironment within these resins. Related studies based on crown ether triphase catalysts are also in progress.

UNIVERSITY OF NEBRASKA
Lincoln, Nebraska 68588

356. STUDIES ON UNUSUALLY REACTIVE METAL POWDERS Reuben D. Rieke Department of Chemistry	$60,000	02-01

We recently discovered that highly reactive metal powders can be prepared by the reduction of metal salts from various organic solvents. Common reducing agents are potassium, sodium, lithium or other reducing agent of high enough potential. The reduction yields the metal in a finely divided state. Metals studied to date exhibit far superior reactivity towards organic and inorganic substrates to that described in the literature for these metals. We recently have shown that this approach will work with transition metals including nickel, palladium, platinum, cobalt, iron, and uranium. We are proposing to study the chemistry of these highly reactive metals. We wish to examine these metals in a variety of oxidative-insertion reactions, preparation of zerovalent derivatives, and catalytic reactions. several new organometallic complexes with potential catalytic activity are proposed. These new catalysts are expected to be useful in hydrogenation reactions, disproportionation reactions, isomerization reactions, and a variety of other reactions.

TEXAS A&M UNIVERSITY
College Station, Texas 77843

357. THE INFLUENCE OF F-ELECTRON CONFIGURATION ON CATALYTIC PROPERTIES OF LANTHANIDE OXIDES Michael P. Rosynek Department of Chemistry	$30,000	02-01

The objective of this research is to correlate variations in catalytic behaviors among the lanthanide oxides with periodic trends in their electronic and magnetic properties. Principal emphasis is being placed on identifying and characterizing the chemical/structural natures, surface densities, and inherent activities of catalytically active sites on these oxides, as well as their responses to varying catalyst preparation and pretreatment conditions. In order to simultaneously probe both the behaviors and interactions of dissimilar surface sites, the diagnostic reactions that are being employed for these studies include conversion of low molecular weight alcohols, primarily ethanol, and decomposition of formic acid, since simultaneous dehydration and dehydrogenation occur for both of these processes over lanthanide oxide catalysts. On La_2O_3, it has been demonstrated that the two reaction pathways for ethanol conversion involve distinct types of catalytic sites that respond differently to varying pretreatment conditions and surface poisons.

WASHINGTON STATE UNIVERSITY
Pullman, Washington 99164

358. METAL CARBONYLS AS HOMOGENEOUS OXIDATION CATALYSTS $60,296 02-01
D. M. Roundhill
Department of Chemistry

The goals of this project are to develop new homogeneous catalysts for the selective oxidation of organic compounds. Reaction pathways are being studied as a means of understanding the features needed in a catalyst for high activity, stability and selectivity. The compounds $Rh_6(CO)_{16}$ and $Re_2(CO)_{10}$ are currently being used for the oxidation of cyclic alcohols and ketones to dicarboxylic acids. Product yields are measured by gas chromatography. Effects on product yield with changing CO pressure have been analyzed. The most recent evidence leads to the conclusion that the metal carbonyls accelerate the decomposition of peroxide intermediates. As a model study the $Re_2(CO)_{10}$ catalyzed decomposition of hydrogen peroxide is being investigated. Experiments are in progress which will probe the mechanistic features of this reaction. Triphenylphosphine and triphenylarsine are also oxidized by molecular oxygen in the presence of $Rh_6(CO)_{16}$. Intermediates are being identified by IR and ^{31}P NMR spectroscopy.

RUTGERS UNIVERSITY
New Brunswick, New Jersey 08903

359. THE NATURE OF ODD-ELECTRON SPECIES AND THEIR ROLE IN CATALYTIC PROCESSES $50,000 02-01
Joseph San Filippo
Department of Chemistry

This program consists of a study of the general chemical and spectroscopic behavior of selected organometallic transition metal radicals and radical anions and the exploration of their role in and possible application to catalytic reactions. Several classes of organometallic radical species are being studied. These include: (1) the products produced by the one-electron reduction of a series of olefin-iron carbonyl complexes; (2) the products formed by the one electron oxidation of selected carbonyl anions (mononuclear, dinuclear and cluster species will be included); and (3) the species produced by the one electron oxidation of alkyl metal carbonylate as well as carbonyl hydride anions. Electron spin resonance spectroscopy is being used extensively to characterize the radicals produced but other techniques including uv-visible, ir and Mössbauer spectroscopy are being used.

UNIVERSITY OF KENTUCKY
Lexington, Kentucky 40506

360. A FUNDAMENTAL STUDY OF CATALYSTS USING LASER RAMAN, INFRARED, AUGER ELECTRON SPECTROSCOPY AND LOW ENERGY ELECTRON DIFFRACTION — $63,000 — 02-01
Gordon A. Sargent
Department of Metallurgical Engineering and Materials Science
E. B. Bradley
Department of Electrical 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 have been used to study the surface structure and bonding of CO, CH_4, H_2 and O_2 adsorbed on Ni(111) and Ni(100) single crystal surfaces. The surface coverage was 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. Thermal desorption experiments have been undertaken for each gas adsorbed on each surface using the linear temperature programming technique. The mars of the desorbed species is determined by means of a precision mars analyzer. The mars analyzer is also used to determine residual gas concentrations in the experimental chamber and to identify the structure of intermediate molecules. Laser Raman and Infrared spectroscopy is used to determine frequency shifts caused by surface structures of the adsorbed molecules and polarization of Raman bonds and changes in bond intensities.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts 02139

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

The ultimate goal of this project is to reduce carbon monoxide catalytically with hydrogen gas to an organic molecule containing two or more carbon atoms such as ethylene, ethylene glycol, etc. The immediate goal is to understand how to reduce carbon monoxide step-wise in model systems employing early transition metals. The project involves preparation and characterization of new hydride and carbonyl complexes and studies of how they react with carbon monoxide and hydrogen, respectively.

Chemical Energy, continued

COLORADO STATE UNIVERSITY
Fort Collins, Colorado 80523

362. PALLADIUM CATALYZED COUPLING REACTIONS: MECHANISM OF REDUCTIVE ELIMINATION $40,000 02-01
J. K. Stille
Department of Chemistry

The objective of this research is to establish the mechanism(s) of reductive elimination of organic groups from palladium complexes in order to gain a better understanding of how carbon-carbon bond formation takes place in catalytic coupling and oligomerization reactions of organic compounds. The 1,1-reductive elimination of ethane from bisphosphinedimethylpalladium(II) complexes takes place by a first order, intramolecular process. Only the cis- isomer undergoes reductive elimination, the trans complex isomerizing to cis prior to the elimination. The mechanisms of reductive elimination from analagous palladium(IV) complexes are also being determined. In an effort to model palladium and platinum metal surfaces, the reductive elimination of alkyl groups from adjacent metal atoms in the simplest analogs, palladium and platinum dimers, is in progress.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

363. A FUNDAMENTAL STUDY OF THE MECHANISM AND KINETICS OF CELLULOSE HYDROLYSIS BY ACIDS AND ENZYMES $90,000 02-01
George T. Tsao, Cheng-Shung Gong, and
Martin Chang - Department of Chemical Engineering

The goals of this project are to gain an understanding of the mechanisms of the regulation of cellulose biosynthesis, the enzyme hydrolysis of cellulose as related to cellulose structure, and the effect of cellulose pretreatment on saccharification. Cellobiase is produced by T. reesei and the Aspergilli constitutively. Extra- and intracellular cellobiases exhibited identical physical and enzymatic properties. Exo- and endocellulases are co-induced by cellulase synthesis inducers. Cellobiase is implicated in the regulation of cellulase biosynthesis and the amounts of cellulases produced extracellularly are determined by secretion as well as by post-translational modification of cellulases. The low activity of cellulases to native cellulose is primarily due to the large crystalline structure of cellulose. Once this is reduced by acid or solvent pretreatment, the susceptibility of the cellulose to cellulases is drastically increased.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

364. METAL CRYSTALLITE SIZE AND SUPPORT EFFECTS ON CO HYDROGENATION — $132,255 — 02-01
24 mo.
FY80-81
M. A. Vannice
Department of Chemical Engineering

This program is oriented toward the long-range goal of improved catalyst systems in general, and better CO hydrogenation catalysts in particular. The objectives in this research are to study the influence of metal-support effects and metal crystallite size on the activity of Pt, Pd, and Ni in the methanation reaction. A unique combination infrared cell/single-pass reactor has been designed and constructed to allow IR spectra to be obtained simultaneously with kinetic data under steady-state reaction conditions. Spectra of equilibrium CO adsorption in the absence of H_2 are being obtained at various temperatures. Specific activities vary by two orders of magnitude as a consequence of the support used, and analysis is presently underway to determine if correlations exist between activity and the different forms of adsorbed CO that can be identified on the metal surface. New kinetic models of the methanation reaction are being examined as a consequence of these recent results which provide information about the state of the working catalytic surface.

PENNSYLVANIA STATE UNIVERSITY
University Park, Pennsylvania 16802

365. GASIFICATION OF DISORDERED CARBONS (CHARS) — $80,195 — 02-01
15 mo.
FY79-80
P. L. Walker, Jr.
Department of Materials Science and Engineering

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. By making measurements on two dissimilar high purity carbons, that is a char and a graphitized carbon black, it is expected that the question of whether there are universal rate constants for the carbon-oxygen reaction will be answered. Companion studies are being conducted in the presence of a 1% loading of platinum. Rate constants will be determined per unit of platinum surface area, using small angle x-ray scattering, and electron microscopy to characterize metal dispersion.

YALE UNIVERSITY
New Haven, Connecticut 06520

366\. ENERGIES OF ORGANIC COMPOUNDS $66,510 02-01
Kenneth B. Wiberg
Department of Chemistry

This project is concerned with the factors which control the energies of organic compounds. Steric effects are being investigated by examining several cases of the interconversion between trigonal and tetrahedral carbons. Specifically, the enthalpies and free energies of hydrolysis of ketals, acetals and orthoesters are being determined and are compared with a commonly used steric parameter. Agreement is found with the free energies but not the enthalpies. A major part of steric effects appears to arise from entropy effects. The hydration of alkenes to alcohols is being studied making use of the reaction of these compounds with trifluoroacetic acid-trifluoroacetic anhydride. The Coulombic contribution to intramolecular interactions is being investigated via calculation of atomic populations derived from extended basis set ab initio calculations.

SRI INTERNATIONAL
Menlo Park, California 94025

367\. ADSORPTION THERMODYNAMICS ON METAL CATALYST SURFACES $65,233 02-01
Henry Wise
Materials Research Laboratory

The goal of this project is to measure the thermodynamics of sulfur adsorption on the catalytically important metal surfaces of Ru, Fe, Co, and Pt. These studies include measurement of sulfur chemisorption on supported and single-crystal surfaces. A closed gas-recirculation system is used to measure sulfur adsorption equilibria on supported metals and Auger electron spectroscopy is used to determine the equilibrium sulfur coverage on single-crystal surfaces following exposure to H_2S/H_2 gas mixtures over a range of temperatures and surface coverages. The results for Ni, Ru, and Fe show that heat of formation of chemisorbed sulfur is very large, much larger than the heat of solution of sulfur and the heat of formation of bulk metal sulfides. Little variation is noted in the heat of adsorption of sulfur on the supported and single-crystal surfaces of Ni and Ru indicating the absence of structure sensitivity. The results obtained are of importance to the problem of metal catalyst poisoning by sulfur species since they provide information about the upper limit of the concentration of sulfur compounds in the feed-stream that can be tolerated for a specified degree of catalyst deactivation.

NATIONAL BUREAU OF STANDARDS
Washington, D. C. 20234

368. STUDY OF HETEROGENEOUS CATALYTIC CHEMISTRY ON TRANSITION METALS $146,200 02-01
J. T. Yates, Jr.
Surface Science Division

Modern surface science methods are being employed to understand model catalytic processes on single crystal surfaces. The synthesis of methane from CO and H_2 over Ni and Ru single crystal surfaces is being studied using a microcatalytic high pressure reactor and Auger spectroscopy. It has been shown that the crystal surfaces yield kinetics of CH_4 formation identical to the kinetics on high area technical catalysts, and the reaction is structure insensitive. Using the single crystals as a model catalyst, quantitative studies of poisoning and promotion are currently underway. In addition the chemisorptive behavior of CO and CH_3OH is being studied on these surfaces using a variety of surface sensitive techniques. These experiments provide a deeper insight into the molecular processes governing surface chemistry.

Separations

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

369. CONTINUOUS CHEMICAL REACTION CHROMATOGRAPHY Rutherford Aris Robert W. Carr, Jr. Department of Chemical Engineering & Materials Science	$37,764	02-02

An experimental investigation of the catalytic dehydrogenation of cyclohexane over Pt/Al_2O_3 will be done in a rotating annulus continuous chromatographic reactor. Particular attention will be paid to conditions for which the reaction can be driven to completion. Comparisons between experimental observations and the predictions of reactor performance by a mathematical model will be made. Experiments on the catalytic dehydration of alcohols are also planned.

An experimental investigation of countercurrent, moving bed reaction chromatography will be initiated. A preliminary study will be done to determine the experimental conditions under which an $A \rightleftharpoons B$ type reaction can be driven beyond equilibrium, and to select candidate chemical reactions. A preliminary reactor design will be done.

BEND RESEARCH, INCORPORATED
Bend, Oregon 97701

370. FUNDAMENTALS OF COUPLED TRANSPORT MEMBRANES W. C. Babcock, R. W. Baker, and J. M. Brooke	$64,599	02-02

The goal of this research program is to develop an understanding of the fundamentals of uranium permeation through coupled transport membranes. These are liquid membranes, consisting of a microporous polymeric support film, and a liquid, water-immiscible complexing agent held within the pores of the support by capillary action. The membrane separates two aqueous solutions. Uranium is extracted into the membrane on one side, it diffuses across the membrane as a complex, and it is released on the opposite side. A number of factors have been found to affect the transmembrane uranium flux. Principal among these are the compositions of the aqueous solutions, the nature of the liquid membrane, and interfacial phenomena such as concentration polarization and interfacial reaction rates.

TEXAS TECHNOLOGICAL UNIVERSITY
Lubbock, Texas 79409

371. METAL ION COMPLEXATION BY IONIC CROWN ETHERS	$40,569	02-02

Richard A. Bartsch - Department of Chemistry
Richard W. Tock - Department of Chemical Engineering

The goals of this research are the preparation of ionic crown ethers and the utilization of these new compounds in selective metal ion complexation. Ionic crown ethers are macrocyclic compounds which bear an anionic group in the proximity of the crown ether cavity. During the current fiscal year, the preparation of these new complexing agents is being pursued. The synthetic methods which are being developed emphasize practicality in order to allow for ease of transfer of promising research results to larger scale applications. When a variety of ionic crown ethers have been prepared, the strength and selectivity of alkali, alkaline earth, and lanthanide ion complexation by these macrocyclic compounds will be assessed.

AMHERST COLLEGE
Amherst, Massachusetts 01002

372. ISOTOPE EFFECTS IN THE SOLUTION OF GASES IN LIQUIDS	$37,490	02-02

Bruce B. Benson and Daniel Krause, Jr.
Department of Physics

This research is directed toward a better understanding of molecular interactions in liquids through studies of isotopic effects in the solution of gases. The heavier isotope in a gas normally is slightly more soluble than the lighter. Mass spectrometric comparison of the isotopic abundance ratios in the dissolved and undissolved gases gives the ratio of the solubilities of the isotopes. Determinations of the dependence of this ratio upon the kind of gas and the temperature are being made in aqueous solutions. The effects of adding various salts to water, and of substituting D_2O for H_2O are being examined, and analyses are being carried out with other solvents such as alcohols, mixtures, and liquids at cryogenic temperatures. The measurements give information about the structure of the solvent and about the interaction of the solute molecules with it.

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

373. FUNDAMENTAL STUDIES IN ISOTOPE CHEMISTRY $117,474 02-02
Jacob Bigeleisen
Department of Chemistry

The goal of this program is to increase and expand our knowledge of the origin and basis of isotope chemistry. Current theoretical work involves correlation of isotope chemistry with molecular forces. Specifically, the isotope chemistry of carbon is being studied through a new perturbation approximation WIMPER. Current studies of the isotope chemistry of hydrogen have led to the discovery of the classification of the isotope chemistry of hydrogen according to the Periodic Table. We call this new result the Periodic System of Isotope Chemistry. Just as the discovery of the Periodic Table of the elements led to the classification of chemistry, we anticipate the development of the Periodic System of Isotope Chemistry will broaden and expand the science of isotope chemistry. Progress is being made in setting up the Stony Brook Laboratory for Isotope Chemistry. Current studies involve isotope effects in liquid-vapor equilibria. These investigations are giving unique information about the liquid state and intermolecular forces.

MINNESOTA, UNIVERSITY OF
Minneapolis, Minnesota 55455

374. PHOTO-INDUCED CATAPHORETIC ISOTOPE SEPARATION $37,764 02-02
J. A. Carruthers
Department of Electrical Engineering

The objective is to demonstrate radiation-induced cataphoretic isotope separation in a gaseous discharge, where separation occurs as a result of selective ionization of one of the gas isotopes which then moves preferentially toward the cathode. Present efforts are concentrated on the Ne^{20} and Ne^{22} isotopes, using He-Ne 0.63 μm laser radiation as a radiation source. A He-Ne^{20} laser tube and a cataphoretic tube are both inside the laser cavity, with the cataphoretic tube containing a mixture of the two neon isotopes. A very sensitive scanning Fabry-Perot spectrometer is used to monitor the neon isotope ratio. A double pumping scheme is being tried using both the laser radiation and fluorescence radiation to pump from the neon metastable level.

BRIGHAM YOUNG UNIVERSITY
Provo, Utah 84602

375. SEPARATION OF ALKALI, ALKALINE EARTH AND RARE EARTH CATIONS BY LIQUID MEMBRANES CONTAINING MACROCYCLIC CARRIERS $55,000 02-02

James J. Christensen
Department of Chemical Engineering

The objectives of this project are to study the metal cation selectivities of synthetic liquid membranes containing macrocyclic ligand carriers and to investigate the use of such membranes in making cation separations. Synthetic macrocyclic ligands of the crown ether and cryptand varieties are initially studied in model "bulk" chloroform membranes to determine which cations are selectively transported and the degree of selectivity which can be obtained. Metal cations under investigation include the alkali metal, alkaline earth and lanthanide cations, as well as Pb^{2+}, Ag^{+} and Hg^{2+}. Separations involving cesium, strontium and the lanthanide (III) cations are emphasized, since these metals are of interest in the nuclear energy field. The most selective macrocyclic ligand carriers are incorporated into liquid surfactant membranes. These membranes offer high surface area for practical membrane separations applications. Stability constants for these metal-macrocyclic ligands are also measured.

UNIVERSITY OF CALIFORNIA/LOS ANGELES
Los Angeles, California 90024

376. MULTIHETEROMACROCYCLES THAT COMPLEX METAL IONS $105,887 02-02

D. J. Cram
Department of Chemistry

The objective of this research is to design, synthesize, and evaluate cyclic organic compounds that selectively complex metal salts and solubilize them in organic solvents. Spherands are the only known ligand systems whose binding of metal cations is driven by the release of electron-electron nonbonded repulsion. They are composed of rigid carbocyclic frameworks that place heteroatoms in a spherical arrangement around enforced cavities. They are the only known synthetic compounds which, in the noncomplexed state, contain holes. Spherands are being studied that are composed of six anisyl units strung together in a ring system by aryl-aryl bonds at their 2,6 positions. They are highly cation selective in forming metallospherium salt complexes of unusual stability. Hemispherands are hybrids of crown ethers and spherands. A large number of structural variants are being prepared and examined which contain anisyl, methoxycyclohexyl, urea, pyridine, pyridine oxide, and amide units.

NAVAL RESEARCH LABORATORY
Washington, D. C. 20375

377. XENON/KRYPTON ELEMENTAL PHOTOCHEMICAL SEPARATION Terence Donohue Laser Physics Branch	$60,000	02-02

Presently employed methods for the separation of rare gases involve high pressures at cryogenic temperatures and are thus costly and inefficient. In this project a photochemical method is used to synthesize xenon difluoride and hence separate xenon from krypton. Fluorine molecules are photodissociated, using either a mercury lamp (366 nm) or an excimer laser (XeCl at 308 nm or KrF at 351 nm). Fluorine atoms, being more reactive than F_2, undergo a sequence of reactions with the rare gas, resulting in the formation of stable molecules. At room temperature, only Xe in a mixture of Xe and Kr will undergo these reactions; the resulting XeF_2 is a solid and precipitates out of the gas, thus separating Xe from Kr. Studies are being made of the extent to which Kr gas is trapped in the lattice of the forming XeF_2, which can reduce separation factors. If the purities can be made large enough, this method can be used to produce a useful Xe product from the radioactive offgases from nuclear reactors and reprocessing plants.

UNIVERSITY OF ARIZONA
Tucson, Arizona 85721

378. CHELATING EXTRACTANTS OF IMPROVED SELECTIVITY Henry Freiser Department of Chemistry	$62,480	02-02

The objectives of this project are to develop reagents of increased selectivity in the separation of the lanthanide metal ions via solvent extraction processes. Mixed ligand chelate extraction of the tervalent lanthanide ions using 8-quinolinol and analogous reagents in conjunction with neutral ligands such as 1,10-phenanthroline are being investigated and the component equilibrium constants are being determined. Preliminary results obtained for such systems indicated that important selectivity via this approach is accessible. New systems will be examined that will exploit the findings to date.

HARVARD UNIVERSITY
Cambridge, Massachusetts 02138

379. ELECTRONIC STRUCTURE OF HELIUM AND HYDRIDE COMPLEXES IN LIQUID TRITIUM Dudley R. Herschbach Department of Chemistry	$45,000	02-02

Theoretical studies of the electronic structure of weakly bound states of helium and hydrogen isotopes are being pursued with the aim of understanding a remarkable experimental observation. The radioactive decay of liquid tritium generates ^3He but the helium remains in solution at concentrations which exceed the known solubility by much more than a factor of a 100. Extensive calculations employing several methods indicate that this "supersolubility" may be due to complexes of the form $He(H^+)(H_2)_n$ with n=2 or greater. Calculations are in progress for a negative counter ion of the form $H^-(H_2)_m$. This work complements an experimental program at Los Alamos. Calculations are also in progress to interpret vibrational spectra of tritiated solids observed at Livermore. Several new lines found in the IR spectra of solid T_2, DT, and tritium-doped D_2 and HT are found to be consistant with calculated frequency shifts for T_2 vibrations and various conformations of T_5^+ and T_3^-. Beam experiments are planned to obtain the energetics of the $H^-(H_2)_m$ complex as a check on the calculations.

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

380. STABLE ISOTOPE STUDIES T. Ishida Department of Chemistry	$105,750	02-02

Vapor pressure differences of isotopic compounds involving $^{13}C/^{12}C$- and D/H-substitutions in fluoromethanes are measured in a precision cryostat with temperature stability of ± 0.001°K, and the results are correlated to molecular forces in the liquid using various liquid models and ab initio molecular force constant calculations. The nitrogen isotope exchange system of nitric oxide (gas)- dinitrogen trioxide (liquid) is studied in a countercurrent flow, packed column system for effects of pressure (up to 10 atmosphere), temperature (0°-30°C), and flow rates upon the height of effective theoretical plates, the holdup, and the separation factor. A new multistage method for a precision determination of isotope separation factor is tested. Theoretical studies being carried out are: (1) Correlation of isotope effects (IE) in terms of a concept of atomic force parameters, (2) Ab initio calculation of IE of frequency shifts upon condensation of non-polar substances, (3) Derivation of explicit correlation between IE and anharmonic vibrational forces.

UNIVERSITY OF GEORGIA
Athens, Georgia 30602

381. MECHANISMS OF HYDROGEN DIFFUSION IN SEPARATION DEVICES M. Howard Lee Department of Physics and Astronomy	$65,395	02-02

The diffusion of Light gases in transition metals exhibits anomalous behavior. The nature of this behavior cannot be understood by classical considerations and must be traced to quantum origin. Our objective is to construct a physical model for hydrogen-in-metals to provide an understanding of hydrogen diffusion in metals. Advances in our knowledge here can have direct bearing on practical applications such as heavy-water enrichment, energy generation by nuclear fusion. Our approach has been to develop a dynamical theory of diffusion via a quantum mechanical model of hydrogen-in-metals. A detailed analysis shows that our model can account for several observed facts. It also makes certain predictions, which now remain to be tested. Under some approximations, our model reduces to well-known limits. As a result, already much of this model is beginning to be known. Our goals are to provide information on the mechanisms of hydrogen diffusion in metals for practical applications already cited.

KENT STATE UNIVERSITY
Kent, Ohio 44242

382. ADSORPTION AND DESORPTION OF HYDROCARBONS AT LOW CONCENTRATIONS Richard Madey Department of Physics	$43,300	02-02

The objectives of this research are to evaluate adsorption and desorption phenomena related to the isothermal transport of low concentrations of hydrocarbons through porous media; to study the physico-chemical aspects of adsorption interference; and to deduce elements of predictability of interest to separation processes. More specifically, the objectives are (1) to investigate the isothermal transport through porous media of single hydrocarbon gases and also binary hydrocarbon mixtures through porous media using saturation, desorption, displacement and inverse-pulse experiments, and to determine the adsorption capacities and heats of adsorption; (2) to analyze the data on the time-dependent transmission (or normalized outlet concentration) in terms of the appropriate mass-transfer models; to determine the effects of interference on the mass-transfer mechanisms, and to analyze the processes underlying the interference effects; (3) to deduce correlations appropriate to scaling, and to evaluate the technical implications in connection with multicomponent operation.

Separations, continued

TEXAS SOUTHERN UNIVERSITY
Houston, Texas 77004

383. SOLVENT EXTRACTION STUDIES USING HIGH-MOLECULAR-WEIGHT AMINES — $39,322 — 02-02
C. W. McDonald
Department of Chemistry

The fundamental goals of this project are to utilize solvent extraction and ion-flotation techniques to develop separation methods for removing metal ions from aqueous solutions. The solvent extraction technique involves the utilization of certain surfactants, particularly high molecular weight amines dissolved in non-polar solvents, as extractants. These high-molecular weight amines react with metal ions to form hydrophobic compounds which are easily extracted from aqueous solutions. The ion-flotation techniques involve somewhat similar chemistry to that of solvent extraction. In ion-flotation, surfactants react with metal ions to form surface active compounds which are floated from aqueous solution as bubbles when air or nitrogen is passed through the solution. A number of high-molecular-weight tertiary ammonium salts show great promise as surfactants for ion-flotation techniques.

UNIVERSITY OF GEORGIA
Athens, Georgia 30602

384. FUNDAMENTAL STUDIES OF SEPARATION PROCESSES — $68,000 — 02-02
L. B. Rogers
Department of Chemistry

Studies are being made in several major areas. First, breakdown of graphitized carbons, carbon blacks, and charcoals by extraction with pentane at elevated temperatures and pressures has shown that both the number and the amounts of soluble compounds decrease on going from graphitized carbons to charcoals. Second, a comparison of the data obtained using three isothermal gas chromatographic columns, each at a different temperature, with that from a single programmed-temperature column indicates that use of the former may sometimes be desirable. Third, the fractionation of sulfur isotopes in carbonyl sulfide and in carbon disulfide has been found to be small but measureable using a column of Porasil A but too small to be detected using a column of Poropak Q. Finally, studies of recycle gas chromatography and of oligomer fractionations using liquid chromatography are also in progress.

SYRACUSE UNIVERSITY
Syracuse, New York 13210

385. MECHANISM OF GAS PERMEATION THROUGH POLYMER MEMBRANES $60,110 02-02
S. A. Stern, S. S. Kulkarni
and G. R. Mauze
Department of Chemical Engineering
and Materials Science

The main objective of this study is to assess the validity of a "free-volume" model of gas transport in and through polymer membranes. Solubility and diffusion coefficients of simple gases, such as CO_2, C_2H_4, and C_3H_8, in polyethylene rods are being measured in a novel apparatus under isothermal-isobaric conditions. Characteristic parameters extracted from these data are used in conjunction with the free-volume model to predict rates of permeation of the gases studied and their mixtures through thin polyethylene membranes. These predictions are being compared with experimental permeation rates determined independently in a high-pressure permeability apparatus. The effects of temperature and pressure on permeability coefficients are of particular interest. Present efforts are directed toward the correlation of the free-volume parameters with basic physicochemical properties of the penetrant gases and the polymer. This study is of both scientific and practical interest, in the latter case for the development of energy-efficient membrane processes for the separation of industrial gas mixtures.

ILLINOIS INSTITUTE OF TECHNOLOGY
Chicago, Illinois 60616

386. STUDIES ON SELECTIVE METAL ION EXTRACTION FOR MULTIPLE ION EXCHANGE REACTIONS IN LIQUID-LIQUID SYSTEMS $48,395 02-02
Lawrence L. Tavlarides
Department of Chemical Engineering

The objectives of the research in hydrometallurgical solvent extraction is to develop the fundamental means to predict selectivity during simultaneous solvent extraction of multiple metal ions when kinetic rates and thermodynamic equilibria both do not favor the desired metal. The system studied is Cu(II), Fe(III) in acid sulfate solutions extracted by β - alkenyl 8 - hydroxy quinoline (Kelex 100) in xylene. Thermodynamic chemical equilibrium studies with Cu(II), Fe(III) and the mixed metals over prescribed temperatures and concentrations are underway. Kinetic studies are in progress employing the Liquid Jet Recycle Reactor to yield data to model the individual metal and mixed metal complexation reactions. Metal compositions are obtained by on line UV-visible spectrophotometry (kinetics) and atomic absorption spectroscopy. A one liter continuous flow stirred tank reactor system with continuous phase separation (employing a high speed centrifuge), on line UV-visible spectroscopy, and photomicrography for drop size measurements is operational for future selectivity extraction studies.

SYRACUSE UNIVERSITY
Syracuse, New York 13210

387. PARTICLE DEPOSITION IN GRANULAR MEDIA $73,813 02-02
Chi Tien
Department of Chemical Engineering
& Materials Science

The ultimate objective of this work is to obtain quantitative understanding concerning the deposition of particles from suspensions flowing through porous media, which can be used as a basis of rational design of deep bed filtration systems. Three major problems are being considered: (1) The development of a generalized correlation of the initial collection efficiency of granular filter beds from the trajectory analysis and the use of the constricted-tube type porous media model, (2) Experimental determination of the collection efficiency of granular filter beds especially the change of the collection efficiency with the increase in deposition and (3) The formulation of a simulation model from theoretical consideration for the study of the deposition dynamics in its entirety.

COLUMBIA UNIVERSITY
New York, New York 10027

388. ISOTOPIC ENRICHMENT USING MAGNETIC ISOTOPE EFFECTS $67,875 02-02
Nicholas J. Turro
Department of Chemistry

The primary goal of this research is to understand the mechanism of reactions whose efficiencies and rates are influenced by nuclear magnetic isotope effects. In general, it appears that many reactions of organic radical pairs that involve a change in electronic spin multiplicity are subject to such effects. The partial photolysis of ketones in detergent solution has been found to result in a striking enrichment in ^{13}C (a magnetic isotope) relative to ^{12}C (a non-magnetic isotope) in recovered ketone. Thus, this method presents a novel and viable procedure for separation of ^{13}C from ^{12}C. The thermolysis of endoperoxides of aromatic hydrocarbons has been found to result in the production of both singlet and triplet molecular oxygen. If the singlet oxygen is selectively trapped, the untrapped triplet molecular oxygen is selectively enriched in ^{17}O. This result is interpreted in terms of a magnetic isotope effect on a diradical intermediate. Since ^{17}O is magnetic, but ^{16}O and ^{18}O are not, a sorting of isotopes via the magnetic isotope effect can operate in diradical intermediates.

UNIVERSITY OF CALIFORNIA/IRVINE
Irvine, California 92717

389. STUDIES ON ISOTOPIC MASS EFFECTS IN CHEMISTRY Max Wolfsberg Department of Chemistry	$68,053	02-02

Theoretical studies of isotopic mass effects on molecular physical and chemical properties are carried out in this project. Most studies of such isotope effects are done within the Born-Oppenheimer approximation; the role of corrections to this approximation is being investigated. Exact calculations of rotational-vibrational energy levels of molecules and isotope effects thereon are necessary for exact theoretical evaluations of isotope effects in chemical exchange processes; such energy levels are being evaluated by diagonalization of the exact Hamiltonian with a large basis set. This study of the exact energy levels is now emphasizing NH_3 and its isotopic variants. Statistical mechanical perturbation theory is being used to illuminate the nature of isotope effects. An investigation is being carried out of how isotope effects on chemical equilibria calculated in the harmonic approximation depend on how the harmonic force constants are deduced from experimental spectroscopic data.

THE AEROSPACE CORPORATION
Los Angeles, California 90009

390. ISOTOPICALLY SELECTIVE, TWO-STEP PHOTODISSOCIATION P. F. Zittel Chemistry and Physics Laboratory	$86,920	02-02

The object of this study is to understand the photophysics, vibrational energy transfer processes, and scavenging chemistry which are important in two-step, photodissociative isotope enrichment. An infrared CO_2 laser pulse is used to selectively promote molecules containing a particular atomic isotope into an excited vibrational state. A subsequent, ultraviolet laser pulse photodissociates vibrationally excited molecules more readily than unexcited molecules. After chemical scavenging, the photodissociation fragments are analyzed mass spectrometrically for yield and isotopic content. A variety of molecules including ozone (O_3) and carbonyl sulfide (OCS) are being studied. Various isotopes of carbon, oxygen and sulfur have been separated using this technique. Important photoabsorption cross sections and kinetic rate constants are deduced from laser absorption measurements and from the effect on product yield and isotope enrichment of varying such experimental conditions as laser timing and sample composition. An extensive computer model of the two-step process is used to interpret experimental results and to predict optimum experimental conditions.

UNIVERSITY OF MASSACHUSETTS
Amherst, Massachusetts 01003

391. DYNAMICS OF HEAT, MASS AND MOMENTUM TRANSFER IN AN INDUCTION PLASMA $53,525 02-03
Ramon M. Barnes
Department of Chemistry

The computer modeling of the flow, temperature, concentration, and radiation distributions in an induction discharge operated at atmospheric pressure under conditions popular when employed as spectral excitation sources is the objective of this project. Computation is based upon solution of steady-state two-dimensional momentum and energy equations in terms of stream function, vorticity and enthalpy simultaneously with one-dimensional electric and magnetic fields equations and their phase difference. Results to date include argon induction discharges over 3 to 27 MHz with flow conditions representative of commercial systems. The effect of aerosol carrier gas flow rate on velocity, temperature, and aerosol concentration fields is being evaluated. The thermodynamic and transport properties of argon, nitrogen, and oxygen at atmospheric pressure from 300 to 20,000 K are being critically evaluated. Experimental verification of model results is proceeding.

UNIVERSITY OF UTAH
Salt Lake City, Utah 84112

392. FOURIER TRANSFORM PHOTOACOUSTIC SPECTROSCOPY $69,989 02-03
Edward M. Eyring
Department of Chemistry

Possible advantages in speed and wavelength accuracy of Fourier transform photoacoustic spectroscopy (PAS) over dispersive PAS in examining opaque solid samples at visible and infrared wavelengths are being explored. Rare earth oxide heterogeneous catalysts are suitable surfaces for these studies since they have highly structured visible absorbance spectra. A Nicolet FTIR spectrometer fitted with a homemade PAS sample cell is being used in the extension of these measurements on catalytic surfaces to infrared wavelengths. Feasibility of making PAS measurements more quantitative by operating at megahertz "chopping" frequencies with piezoelectric detectors is also being investigated. A potentially interesting high frequency light source for such measurements is the white light at visible or infrared wavelengths from a synchrotron. Electronics for such a synchrotron PAS experiment are being constructed and tested with a high frequency pulsed dye laser.

CITY UNIVERSITY OF NEW YORK/BROOKLYN COLLEGE
Brooklyn, New York 11210

393. APPLICATIONS OF NUCLEAR AND RADIOCHEMICAL TECHNIQUES IN CHEMICAL ANAYLSIS $49,934 02-03
Harmon L. Finston and Evan T. Williams
Department of Chemistry

Major goals of this investigation are the development of sample pretreatments tracer techniques,and concentration methods for the analyses of environmental and geological samples for trace constituents by proton induced x-ray emission, (PIXE) by electrochemical methods, spectrochemical methods and nuclear and radiochemical methods in general. Preparation of samples for PIXE analysis and calibrations are performed by fusion, acid dissolution, and also by a "Schoniger" combustion technique developed in this laboratory. The latter technique involves freezedrying, grinding, pressing into a cylinder and combustion in a flask filled with oxygen and containing an appropriate solution for dissolution of the residue. Liquid-liquid homogeneous solvent extraction of a variety of mono- and bidentate metallic ion complexes into propylene carbonate is being applied for separation, concentration, and determination. Surfactants which are miscible with water at room temperature and immiscible at elevated temperatures (just opposite to the behavior of propylene carbonate) are also being studied.

PURDUE UNIVERSITY
West Lafayette, Indiana 47907

393a. REACTIONS OF METAL IONS AND THEIR CLUSTERS IN THE GAS PHASE USING LASER IONIZATION-ION CYCLOTRON RESONANCE SPECTROSCOPY $60,000 02-03
Ben S. Freiser
Department of Chemistry

We plan to study the application of solution chelates to chelation in the gas phase to be used to selectively form gaseous molecules. The study of such gaseous chelates can be useful in their own right from an analytical standpoint and may also shed light on some little understood solution properties. In addition the gas phase chemistry will be mainly for ions in an "unusual" oxidation state not observed in aqueous solution, e.g., Fe^+. The plan includes the study of the use of metal ions as chemical ionization reagents for differentiating complex mixtures.

THE AEROSPACE CORPORATION
Los Angeles, California 90009

394. LASER-EXCITED NONRESONANT FLUORESCENCE SPECTROSCOPY | $53,000 | 02-03
J. A. Gelbwachs
Analytical Spectroscopy Section

Laser induced nonresonant 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. Excited state population redistribution in atoms that undergo collisions with various partners will be investigated with particular emphasis being placed on the study of vibrationally resonant transfer between excited atoms and molecules along with the spin selectivity of the collision processes. 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 simple molecules.

UNIVERSITY OF MARYLAND
College Park, Maryland 20742

395. NON-DESTRUCTIVE DETERMINATION OF TRACE-ELEMENT CONCENTRATIONS | $105,000 | 02-03
Glen E. Gordon, William H. Zoller
and William B. Walters
Department of Chemistry

A new method of non-destructive analysis for many of elements in coals, rocks, fly ash, waste streams, oils, atmospheric particles and other energy related materials is under development: neutron-capture prompt γ-ray activation analysis, PGAA. Samples are irradiated in a neutron beam from the National Bureau of Standards (NBS) reactor. Prompt γ rays emitted during irradiations are observed with a high resolution germanium detector. Many materials and standards have been irradiated in order to identify γ rays emitted by the various elements which are intense enough for use as analytical measurements. Gamma rays from the following elements are observable in most of the materials noted above: H, B, C, N, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, N, Fe, Cd, Nd, Sm and Gd. The reliability of the method for these elements has been tested by analysis of NBS Standard Reference Materials (SRMs) including several coals and fly ashes, orchard leaves and bovine liver. Extensions of the method to a wide range of rocks, oils, oil shales and other petroleum-related samples are under study.

UNIVERSITY OF VIRGINIA
Charlottesville, Virginia 22901

396. THE GLOW DISCHARGE AS AN ATOMIZATION AND IONIZATION SOURCE W. W. Harrison Department of Chemistry	$50,201	02-03

This project is a study of the glow discharge as an atomization and ionization source in analytical chemistry. Of interest is the development of the discharge as a source for the trace element analysis of solids by mass spectrometry. We have coupled the discharge to a quadrupole mass filter to obtain a relatively simple mass spectrometer. We are determining the optimum design for the ion source and studying several fundamental aspects of discharge sputter/atomization/ionization processes. Multielement analysis procedures are being developed for solids and solution samples.

UNIVERSITY OF WYOMING
Laramie, Wyoming 82071

397. SOLID SURFACE LUMINESCENCE ANALYSIS Robert J. Hurtubise Department of Chemistry	$58,989	02-03

The main goals of this project are to elucidate the experimental conditions and solid surface interactions needed for strong luminescence signals from organic compounds adsorbed on the surfaces, and to develop further the analytical potential of this approach for organic trace analysis. Several alkylphenols and other phenolic types are being adsorbed on polyacrylic acid-NaCl mixtures and other polymer-salt mixtures 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, and surface area experiments. Similar work is being conducted with organic nitrogen compounds except other solid mixtures such as silica gel with an organic binder are being used to induce luminescence signals.

OHIO STATE UNIVERSITY
Columbus, Ohio 43210

398. DEVELOPMENT AND OPTIMIZATION OF METHODOLOGIES FOR ANALYSIS OF COMPLEX HYDROCARBON MIXTURES $59,939 02-03
R. J. Laub
Department of Chemistry

The fundamental goals of this project are the development of gas-chromatographic methodologies for the separation and identification of complex hydrocarbon mixtures, and the study of fabrication of microbore liquid-chromatographic columns of ultra-high efficiency. In addition, criteria for the quantitative optimization of LC mobile-phase composition, choice of column temperature, and solvent gradient are also being examined. One of the most useful strategies in separations is employment of mixed phases, and it has thus far been determined that GC retentions with mechanically-mixed packings in fact correspond precisely to those predicted from the relevant pure-phase partition coefficients. Entire spectra of solute/solvent interactions can hence be examined with only two (pure-solvent) gas-chromatographic runs. Further, retentions with solvents of intermediate selectivity can be duplicated with mixtures of other sorbents and so, a set of a half-dozen or so standard liquids can be defined which supplant the 500 or so stationary phases currently extant in GC.

NATIONAL BUREAU OF STANDARDS
Washington, D. C. 20234

399. QUANTITATIVE OF FOSSIL FUELS BY MASS SPECTROMETRY $104,000 02-03
L. Wayne Sieck
National Measurement Laboratory

The goal of this project is to develop sub-minute mass spectrometer 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, as well as the reactivity and selectivity of other reagent ions, are in progress.

Chemical Engineering Sciences

STANFORD UNIVERSITY
Stanford, California 94305

400. TRANSPORT CHARACTERISTICS OF SLURRIES IN PIPELINES: FLOW REGIMES AND PRESSURE DROP $150,000 02-04
Andreas Acrivos 36 mos.
Department of Chemical Engineering FY80-82

The objective of this research is to develop, from a fundamental point of view, methods for (1) predicting the pressure drop and (2) delineating the various flow regimes of slurry flow in pipelines. The research is based on the equations of continuum mechanics for two-phase materials which are solved by using asymtotic techniques. This research addresses the effects of particle-particle interactions in slurry flows in order to improve the pressure drop predictions of two-phase flow systems.

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

401. CHEMICAL REACTIONS AND TURBULENCE $51,991 02-04
R. Chevray
Department of Mechanical Engineering

High quality data are sought for a well-defined turbulent situation - a two-dimensional mixing layer - in which we have chemical reactions with a known simple kinetic scheme. Additional complexities of finite heat release are avoided by use of small concentrations for the reaction chosen ($NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu + O_2$). Large Reynolds numbers, small dilution numbers, large reaction speed numbers and several concentration ratios are investigated. Conditional as well as usual measurements are made of separate and joint statistics of the velocity and concentration 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.

STANFORD UNIVERSITY
Stanford, California 94305

402. FUNDAMENTAL STUDIES OF FLUID MECHANICS AND TRANSPORT IN POROUS MEDIA $50,000 02-04
George M. Homsy
Department of Chemical Engineering

The objective of this work is to understand two problems in porous media; that of natural convection heat transfer and of the flow of non-Newtonian fluids in porous materials. In the first, computer solutions are being generated which address the question of non-uniqueness of convection patterns of interest in geothermal reservoir engineering. In the second both theory and experiment are being used to understand the flow-pressure drop relationship for well-characterized non-Newtonian aqueous solutions of polyisobutylene. The relationships are of interest in tertiary oil recovery.

NATIONAL BUREAU OF STANDARDS
Washington, D.C. 20234

403. TRANSPORT AND PHASE EQUILIBRIA IN MULTICOMPONENT FLUIDS $73,596 02-04
18 mo.
FY79-80
John M. Kincaid
Statistical Physics and Materials Theory Group

The purpose of this project is to develop and implement simple, accurate techniques to treat the transport and phase transition properties of multicomponent, multiphase 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 difussion coefficients for hard-sphere mixtures using the Revised Enskog theory (2); and a molecular dynamics study of diffusion in binary hard-sphere mixtures is being used to calibrate the RET (3).

UNIVERSITY OF CALIFORNIA/DAVIS
Davis, California 95616

404. STATISTICAL MODELLING OF CHEMICALLY REACTING TURBULENT FLOWS	$53,634	02-04
Brian E. Launder	17 mo.	
Harry A. Dwyer	FY79-80	
Department of Mechanical Engineering		

The project aims to develop a mathematical model for the interesting statistical properties of turbulent reacting flows, especially of turbulent flames. Research in this initial period of funding is directed at clarifying and resolving certain poorly understood aspects of non-reacting flows which also play an important role in flames. One of our current studies is the inert mixing of helium and nitrogen for which different approaches to the treatment of density fluctuations are being tested and assessed. One attractive scheme, devised in the present work, is an asymmetric mass weighting of the velocity which achieves the compactness of conventional mass averaging while retaining the clarity of the physical processes usually associated with volume averaging. Other active studies concern the further development and application of closures with two or more independent turbulent time scales with which to characterize the mixing processes.

NATIONAL BUREAU OF STANDARDS
Boulder, Colorado 80303

405. INTEGRATED EXPERIMENTAL AND THEORETICAL STUDY OF THE THERMOPHYSICAL PROPERTIES OF FLUID MIXTURES	$125,000	02-04
Niel A. Olien	15 mo.	
Thermophysical Properties Division	FY80-81	

The long range goals of this program are the development of generalized techniques which accurately predict the thermophysical properties of fluid mixtures and to gain a fundamental understanding of fluid behavior. The approach is an integrated program involving experimental measurements, theoretical studies (conformal solution theory), correlation and equation of state work as well as computer simulation studies. Initial efforts center on conformal solution theory and especially on generalizing an existing extended corresponding states mixtures model. The latter work involves extending the existing model to include the entire fluid PVT surface. The system studied is the methane-nitrogen system for which extensive new experimental data are available. A new high temperature PVT apparatus is nearing completion and will be used in the near future to provide needed experimental data on carefully selected binary systems.

Chemical Engineering Sciences, continued

UNIVERSITY OF PENNSYLVANIA
Philadelphia, Pennsylvania 19104

406. THERMOCHEMICAL PROCESSES FOR HYDROGEN PRODUCTION BY WATER DECOMPOSITION $-0- 02-04
Daniel D. Perlmutter
Department of Chemical and Biochemical Engineering

This project includes systematic study of the several physical and chemical contributions to the kinetics of gas-solid reactions, with the longer-range goal of designing reactors to be part of proposed thermochemical cycles. Results to date include several models for solid phase and solid-fluid reactions, emphasizing (i) a population balance approach, (ii) an equilibrium-interface, and (iii) a random-pore distribution. Closer to practical design, experimental work has been done on solids mixing in a rotary reactor and on solids decomposition rates. Using these results, a simulation study has been carried through to predict conversion and temperature profiles in rotary chemical reactors and to indicate the relative sensitivities of the reactor behavior to the major manipulative variables.

UNIVERSITY OF CALIFORNIA
Santa Barbara, California 93106

407. SUPPORTED LIQUID-PHASE CATALYSIS $41,701 02-04
Robert G. Rinker
Department of Chemical Engineering

The basic goal of this research is to obtain a fundamental understanding of the coupled mass transfer and chemical reaction of gaseous species in liquid homogeneous catalysts which are supported as thin films in porous solids. An isomerization reaction between gaseous quadricyclene and norbornadiene is being used to test general as well as specialized mathematical models describing supported liquid-phase catalysts (SLPC). The liquid isomerization catalyst being used in the tests is cobalt-tetraphenylporphorynchloride dissolved in 1-chloronaphthalene which in turn is supported as a thin film on the pore walls of macroporous aluminum oxide pellets. The support immobilizes the catalyst and provides a large surface area for increasing reaction rates in transport-limited systems. A problem of liquid-film swelling is being experienced, and several approaches for eliminating it are being considered, including cyclic operation, raising the temperature, and decreasing the solubility of reactants and products in the liquid catalyst. Applications of SLPC to homogeneously-catalyzed hydrogen production from water and to coal liquifaction are being considered.

NORTH CAROLINA STATE UNIVERSITY
Raleigh, North Carolina 27607

408. DYNAMIC MEASUREMENTS OF TWO-PHASE FLOW PHENOMENA USING NMR TECHNIQUES R. F. Saxe Department of Nuclear Engineering	$62,415	02-04

The objects of this project are to develop equipment which can measure the characteristics of two-phase flow as a function of time and of space within a reasonably large volume and to analyze the resulting characteristics as fluctuation phenomena. The measurement technique will utilize the NMR characteristics of water to measure void volume and the use of a linear magnetic field gradient will allow the study to be conducted as a function of space. Repetitive scanning or Fourier transform techniques will allow the required time resolution to be obtained. The investigation of two-phase phenomena as fluctuation phenomena is important if transients are to be understood and computer calculations are to be verified.

UNIVERSITY OF MINNESOTA
Minneapolis, Minnesota 55455

409. FUNDAMENTAL HEAT TRANSFER PROCESSES RELATED TO PHASE CHANGE THERMAL STORAGE MEDIA E. M. Sparrow and J. W. Ramsey Department of Mechanical Engineering	$56,370	02-04

The basic goal of this project is to investigate the fundamental heat transfer processes which occur in phase-change thermal storage systems, with the ultimate objective of providing information which would enable more effective design of energy storage devices. Heat transfer in both freezing and melting is being investigated. For freezing, a basic discovery resulting from the research is that under certain circumstances, freezing can be drastically retarded and even terminated by natural convection. Under other operating conditions, the dominance of natural convection in the freezing process ultimately gives way to a freezing mode controlled by heat conduction in the solidified material. For melting, natural convection is found always to occur. The natural convection accelerates the rate of melting.

Chemical Engineering Sciences, continued

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

410. TRANSPORT PROPERTIES OF MULTIPHASE SYSTEMS G. Stell Department of Mechanical Engineering	\$75,000 18 mo. FY79-80	02-04

The overall aim of this project is the development of a microscopic transport theory of multicomponent and multiphase systems. A general variational kinetic theory based upon the maximization of entropy has been developed. It provides a lowest-order approximation from which analytic expressions for transport coefficients are being derived and evaluated. The theory has been extended for solute-solvent systems to yield correct hydrodynamic limits when the solute-solvent size ratio goes to infinity. Finally a study has been initiated to characterize the structure of porous media in terms of n-point probability densities that enter the transport coefficients describing flow through such media.

CORNELL UNIVERSITY
Ithaca, New York 14853

411. EXPERIMENTAL & THEORETICAL STUDIES OF DENSE FLUID MIXTURES W. B. Street and K. E. Gubbins School of Chemical Engineering	\$163,643 24 mo. FY80-81	02-04

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

412. DYNAMICS OF VAPOR EXPLOSIONS $36,790 02-04
B. Sturtevant
Department of Chemical Engineering

The explosive vaporization of a volatile liquid heated to its limit of superheat is being studied for the purpose of understanding the rapid transport and dynamical processes which occur during the early stages of explosion when departures from thermodynamic equilibrium are very large. The rapid vaporization of single spherical droplets of butane, about 1 mm in diameter, immersed in a host liquid (ethylene glycol) are studied in a bubble column apparatus using high-speed photography and far-field pressure measurements. An unexpected instability of the evaporating liquid-vapor interface has been discovered. In addition, peculiar, rapidly propagating wave patterns are observed on the non-evaporating interface between the butane vapor and the host liquid after the bubble grows to meet a portion of the butane drop wall. Finally, the pressure measurements suggest that the bubble grows in an oscillatory fashion. The effect that these processes have on the observed rate of vaporization of superheated liquids is presently being examined

BES 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 1980 Equipment Funds were assigned as follows.

	Equipment Funds (K$)
Ames Laboratory	180
Argonne National Laboratory	575
Bartlesville Energy Technology Center	10
Brookhaven National Laboratory	797
Idaho National Engineering Laboratory	10
Lawrence Berkeley Laboratory	475
Lawrence Livermore National Laboratory	25
Los Alamos National Scientific Laboratory	55
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Notre Dame Radiation Laboratory	150
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Department of Energy
Washington, DC 20545