

Summaries of FY 1978 Research in the Chemical Sciences

April 1979

U.S. Department of Energy

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

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FOREWORD

This report documents the Chemical Sciences basic energy research program of the Department of Energy. In this program, scientists at government, university, and private sector corporate laboratories conduct research on fundamental interactions, processes, and techniques which are deemed at least potentially important in the conversion, storage, and efficient use of energy. The goal is to discover and make available new scientific knowledge, essential knowledge that will contribute to improvement of the national energy posture.

The program includes research bearing on areas such as: coal chemistry, catalysis, hydrogen, combustion, solar photoconversion, fusion energy, atmospheric chemistry and magnetohydrodynamics. The research is conducted generally by chemists, physicists and engineers. Predecessors of the program were carried on as part of the research programs of the Atomic Energy Commission and the Energy Research and Development Administration. The latter was incorporated into the Department of Energy during 1977.

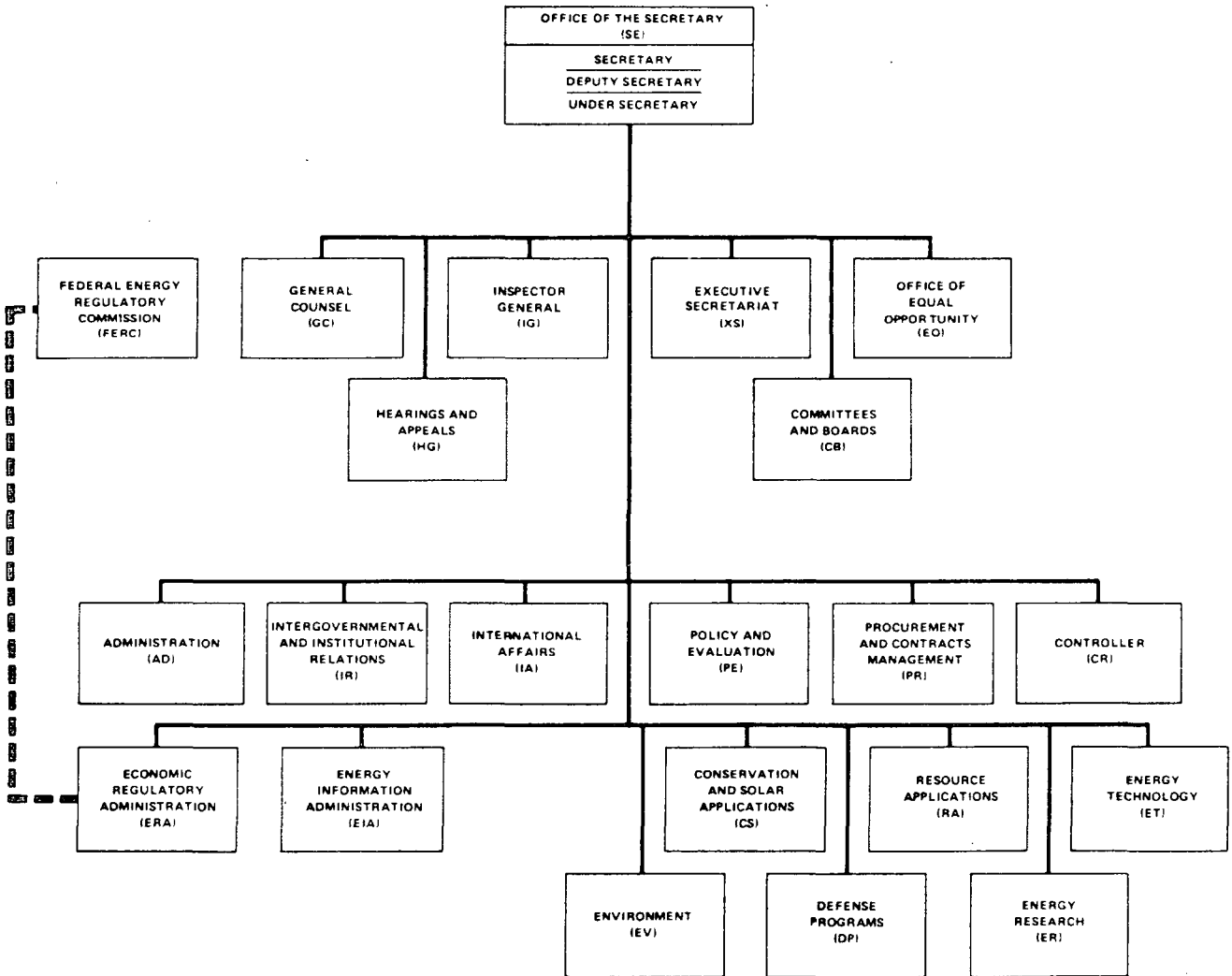
The Department of Energy (DOE) was officially activated on October 1, 1977. Thus this report covers the first full year of operation under the aegis of the DOE. The main organizational structure of the DOE is shown on page iv. The Chemical Sciences basic energy research program now constitutes the program of the Chemical Sciences Division under the Associate Director for Basic Energy Sciences in the Office of Energy Research.

Other divisions under the Associate Director for Basic Energy Sciences, namely, the Divisions of: Materials Sciences; Nuclear Sciences; Engineering, Mathematical and Geosciences; Advanced Energy Projects; and Biological Energy Research each conduct a separately identified basic energy research program. Thus the Chemical Sciences program constitutes only one portion of a wide range of research supported by the DOE Office of Energy Research.

This report contains summaries of all Chemical Sciences research projects underway in FY 1978 and provides a summary of funding levels together with appropriate indexes.

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

DEPARTMENT OF ENERGY HEADQUARTERS ORGANIZATION



INTRODUCTION

The purpose of this report is to provide a convenient, indexed compilation of the individual research projects that make up the DOE Chemical Sciences basic energy research program. The report should prove useful to legislators, administrators, managers and scientists concerned with the implementation and coordination of energy and other research projects and programs.

Section A of the report lists all of the DOE in-house projects; section B lists all of the projects supported at university and other non-DOE laboratories. Section C is an analysis and summary of funding levels. Section D includes the various indexes.

Each project carries a number for reference purposes. The project title, funding level, budget number (e.g. 01-1), and the names of the principal investigators are given for each project along with the summary description of the project. The first two digits of the budget number refer to either Fundamental Interactions (01) or Processes and Techniques (02). The budget numbers carry the following titles for FY 1978:

- 01-1 - Photochemical and Radiation Sciences
- 01-2 - Chemical Physics
- 01-3 - Atomic Physics

- 02-1 - Chemical Energy
- 02-2 - Separations
- 02-3 - Analysis
- 02-4 - Chemical Engineering Sciences

The project summaries were prepared by the Chemical Sciences Division technical staff from summaries provided and/or other project documentation as required. It should be recognized that it is impossible to include all of the technical data available for such a wide variety and large number of research projects. By the time the information could be compiled it would be outdated. The approach taken was to briefly describe the actual scope of each project in FY 1978. The best method for obtaining more detailed information about a given project is to contact directly the investigators listed. Chemical Sciences Division staff assignments are shown on page vi and staff members may be contacted at the phone numbers listed.

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Washington, D.C. 20545

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SECTION A
DOE LABORATORIES

The information in this section was taken from current DOE Laboratory program budget submissions. Most of these projects are of a continuing nature.

AMES LABORATORY
Iowa State University
Ames, Iowa 50011

Chemical Sciences - Fundamental Interactions

H. J. Svec - Phone: (FTS) 865-6487 or (515) 294-6486

V. A. Fassel - Phone: (FTS) 865-2112 or (515) 294-2112

1. PHOTOCHEMISTRY AND SPECTROSCOPY \$ 84,000 01-1
 G. Small

The structures, photophysics and photochemistry of organic molecules and their solids. Projects include: fundamental light absorption and electronic energy transfer mechanisms in solids; development of laser based methodologies for probing the structure of amorphous solids (glasses); solid state isotopically selective photochemistry; and electron-vibration interactions in polyatomic molecules and solids. Conventional optical and laser spectroscopic methods are most often used. The program includes energy related problems which can be solved using recent advances in chemical physics. Specific examples involve research on organic free radicals important in combustion processes and the characterization and quantitation of fossil fuel produced organic pollutants.

2. RADIATION AND SOLID STATE \$ 12,000 01-1
 SPECTROSCOPY
 D. Martin

Chemical fate of radioactive nuclides formed in solid, inert covalently-bonded compounds of transition-metal elements, including cluster compounds with metal-metal bonds. Szilard-Chalmers processes; chemical changes in the radioactive components upon thermal or radiation annealing, kinetic parameters for defect-induced reactions; activation energies for the transfer of defect-energy by promotion of trapped electrons into the conduction band together with the dependence of such energy transfer upon structural and compositional factors.

AMES LABORATORY

Chemical Sciences - Fundamental Interactions (Continued)

5. MASS SPECTROSCOPY-ION SOURCE CHEMISTRY \$ 72,000 01-2
H. Svec, G. D. Flesch

Chemistry of inorganic, organometallic and organic compounds occurring in the ion sources of mass spectrometers; development, in conjunction with studies of chemical reactions occurring in these ion sources, of special instruments which detect ions and their complementary neutral fragments simultaneously.

6. MOLECULAR BONDING THEORY \$191,000 01-2
K. Ruedenberg, S. Elbert

Theoretical calculations to obtain useful descriptions of reactive molecular changes; in particular investigation of energy barriers and activation energies. Development of rigorous and general, yet practicable and efficient quantum-mechanical ab-initio methods beyond the single-configuration self-consistent-field approach. Quantitative analyses of electronic rearrangements along reaction paths in particular for transition states. Establishment of their relationships to reactive energy changes and deduction of interpretative implications for reaction energetics and kinetics. Investigation of reactions involving small and medium sized molecules; application to reactions occurring in the atmosphere and during combustion.

7. ATOMIC MOLECULAR AND FREE RADICAL CROSSED BEAM KINETICS \$113,000 01-2
C. Ng

Combustion chemistry by molecular beam studies, photoionization mass spectrometry; intermediate radicals, stable products and ions in flames; high resolution photoionization of molecules and transient radicals; low pressure pyrolysis of hydrocarbons; product channels and energy of single collision processes; molecular dynamics of excited atoms and molecules; energy distributions in products by laser induced fluorescence and chemiluminescence; ion-molecule reactions.

AMES LABORATORY

Chemical Sciences - Processes and Techniques (Continued)

11. PROPERTIES OF RARE EARTH ELECTROLYTES
F. Spedding
- \$ 22,000
- 02-1

Basic studies of aqueous solutions of electrolytes taking advantage of the special property of the rare-earth cations which predominately change cation size only. This limits the number of parameters and hopefully will shed light on water itself which is one of the most complicated common solvents. The aim of the studies is to gain a fundamental understanding of electrolyte solution chemistry.

12. METALLIC AND INORGANIC HYDRIDES
R. Barnes, J. Corbett
- \$120,500
- 02-1

Structural and electronic properties for high hydrogen affinity and capacity. Chemistry-physics-metallurgy of metal-hydrogen interactions for hydrogen storage. LaNi_5 and other RE-transition metal compounds and alloys, low-valent Group IV and V metal compound matrices, metal cluster compounds. Enthalpy and free energy of H_2 uptake; low-temperature heat capacities; structure by X-ray, neutron diffraction, NMR; partial molal volumes, hydrogen interaction parameters; hydrogen mobility by NMR and kinetics; UPS and XPS measurements.

13. THERMOCHEMICAL CYCLES FOR THE PRODUCTION OF HYDROGEN FROM WATER
D. Ulrichson, D. Martin
- \$ 58,500
- 02-1

Investigation of chemical materials and cyclic reaction systems for the decomposition of water into hydrogen and oxygen. Study of thermodynamic properties and kinetic behavior at temperatures up to 1200°K of reaction steps common to several thermochemical cycles, e.g. oxygen generation by chlorine. Comparative evaluation of reactor designs and costs for such steps with particular emphasis on reactions involving solids and the development of rate models which account for structural change of the solid as reaction proceeds.

AMES LABORATORY

Chemical Sciences - Processes and Techniques (Continued)

14. DIFFRACTION STUDIES OF COAL STRUCTURES
J. Clardy
- \$ 53,500
- 02-1

X-ray diffraction study of coal and related materials to obtain information not available from earlier powder x-ray studies. Ordering in coal (two dimensional) and derived polymeric liquids (one dimensional), studies made with oriented fibers and films. Study of plausible coal precursors (e.g., peat and lignin).

15. COAL CHEMISTRY AND CHARACTERIZATION
T. Squires, T. Barton
- \$ 33,000
- 02-1

Heteroatoms (S,N,O) in coal structures - characterization of structural aspects by silylation reactions using chemical and NMR methods. Methods for degradation of coal. Basic structures of organosulfur subunits.

16. ION EXCHANGE METHODS FOR SEPARATIONS
J. Powell
- \$130,000
- 02-2

Cation-exchange and extractive systems to produce pure (natural) lanthanides and to partition actinides and lanthanides for management and possible utilization of nuclear wastes. Synthesis of new chelatants and chelates including those having hydrophobic and organophilic properties. Study of chelatant and chelate stabilities, separation factors, synergism and kinetics related to the isolation of actinides and lanthanides. Investigation of the feasibility, mechanisms, economics and kinetics of the removal of alkali-metal cations from peat, lignite and other low-rank coals to alleviate fire-side boiler-tube fouling in fossil-fueled power plants.

AMES LABORATORY

Chemical Sciences - Processes and Techniques (Continued)

17. ANALYTICAL SPECTROSCOPY \$301,000 02-3
V. Fassel, R. Kniseley,
A. D'Silva, W. Haas

Basic science, methods, and hardware for inorganic trace and ultratrace analyses for present and predicted energy, environmental, biomedical problems. Inductively-coupled plasma excitation sources for atomic emission spectroscopy; optical emission from selective X-ray-induced energy transfer to trace activators in solid state materials; photoacoustic spectroscopy, especially on coal, solar conversion and energy conservation materials.

18. ANALYTICAL SEPARATIONS \$ 68,000 02-3
J. Fritz

New chemical analyses and separations, particularly chromatographic, for direct use and for analytical support of other research. Organics; simplified analyses of trace organic substances in water, related to fossil fuels. Development of highly selective chelating resins for metal ions; applications in chemical analysis, waste removal, and recovery of valuable metals.

19. ANALYTICAL MASS SPECTROSCOPY \$166,000 02-3
H. Svec, R. Conzemius,
G. Junk

Contamination-free trace impurity analyses by mass spectrometry with minimal sample manipulation; spark source with or without isotope dilution for solids; focussed laser-d.c. arc ion source for small areas or bulk sampling by rastering; hollow-cathode discharge ion source for analyzing frozen untreated aqueous solutions; gas chromatography-mass spectrometry-extraction for organic impurities in water and gases.

AMES LABORATORY

Chemical Sciences - Processes and Techniques (Continued)

20. ACTIVATION ANALYSIS \$ 45,000 02-3
A. Voigt

Application of neutron activation and capture gamma ray analysis to problems related to the direct utilization of coal. Investigation of use of californium-252 sources to monitor coal impurities: sulfur, iron, moisture in coal streams for potential use in coal preparation plant. Demonstration of use of Cf-252 neutrons for capture gamma ray determination of other elements, e.g., chlorine, in on-line applications.

21. LASERS IN ANALYTICAL \$190,000 02-3
CHEMISTRY
E. Yeung, G. Tejwani

Identification and demonstration of improved analytical sensitivity and reliability through use of lasers. Development of Fabry-Perot detection (atomic emission from spark sources) and laser-excited atomic fluorescence for improved sensitivity in element detection; new detectors for liquid chromatography for organics in fossil fuels; finding paths of trace elements and organics in pollution studies; Raman methods for combustion diagnosis; optimization of diode laser measurements at actual source of air pollution from fossil fuel utilization; long-path pollution monitoring, remote sampling.

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

Chemistry Division

P. R. Fields - Phone: (FTS) 972-3570 or (312) 972-3570
J. Unik - Phone: (FTS) 972-3571 or (312) 972-3571

22. RADIATION CHEMISTRY OF SOLUTIONS \$414,000 01-1

M. S. Matheson, C. D. Jonah, J. R. Miller
S. Gordon, M. C. Sauer, A. D. Trifunac,
K. H. Schmidt, J. C. Sullivan, W. A. Mulac

Basic studies of energy deposition mechanics and fast chemical processes associated with passage of ionizing radiation through solutions. Research includes electron solvation mechanism in polar and non-polar liquids, reactions of dry electron and dry hole (H_2O^+), decay rates of e^- and OH as a consequence of inhomogeneous deposition of energy by ionizing radiation, behavior of ions and excited states in hydrocarbons, search for new shortlived intermediates, comparison of redox behavior of lanthanide and actinide ions, pulse radiolysis using high linear energy transfer ions, and activation energies for reactions between radiolytic products of water. This research is based upon use of the ANL Electron Linac with its unique high-current, picosecond beam widths and associated instrumentation.

23. FUNDAMENTAL CHEMICAL PROCESSES STUDIED WITH RADIATION CHEMICAL PROBES \$384,000 01-1

M. S. Matheson, J. R. Miller, A. D. Trifunac,
K. W. Johnson, M. C. Sauer

Fundamental processes under study are: electron tunneling through rigid solvents, magnetic field effects on radical-radical interactions in liquids, and energy transfer in gases. Rates of intermolecular electron tunneling (10 to 40 Å through inert solvent) are studied as a function of reaction exothermicity, molecular structure, solvent ion states and temperature. Time-resolved epr and chemically induced dynamic electron polarization (CIDEP) are used to study transient radicals generated by pulse radiolysis of solutions. Observations provide details of radical structure, radical-radical interactions, and reaction mechanisms. Chemical induced dynamic nuclear polarization (CIDNP) observed in products with flow Fourier Transform NMR defines precursors of products and provides information on radical interactions and reactions. Deposition and migration of energy, ion recombination and excited state kinetics are studied in pulse-radiolyzed rare-gas and rare-gas-halogen mixtures.

ARGONNE NATIONAL LABORATORY
Chemistry Division (Continued)

24. PHOTOCHEMISTRY AND CHEMICAL STORAGE OF SOLAR ENERGY \$228,000 01-1
M. S. Matheson, A. D. Trifunac, C. D. Jonah
J. R. Norris, M. C. Thurnauer

Aqueous photochemical systems are being studied, seeking principles and components which could lead to successful chemical storage of solar energy. Improved photoredox systems are being developed by (1) accelerating forward electron transfer reactions; (2) enhancing the initial separated-charge yield; and (3) inhibiting back reactions. $(CT)Ru(bpy)_2^{2+}$ is currently used in microheterogeneous systems (micelles, monolayers, polyelectrolytes and vesicles) to achieve these improvements and searches for better photoredox pairs are underway. Research is also directed to photo-generating H_2 from H_2O with metal-ion complexes, reducible by one-electron transfer from a photosensitizer. The reduced form then transfers two electrons to water to give H_2 . The ANL Electron Linac and pulse radiolysis techniques are used to simplify the study of photochemical energy storage, by producing short-lived redox intermediates in the absence of photosensitizers.

25. COMBUSTION AND ATMOSPHERIC POLLUTION CHEMISTRY \$334,000 01-1
S. Gordon, K. H. Schmidt, M. C. Sauer
W. A. Mulac, C. D. Jonah

Pulse radiolysis with time-resolved spectroscopic detection is used to study reactions of free radicals in the gas phase and to measure reaction rate constants under a wide variety of controlled conditions of temperature and pressure in the presence of different third body gases. With the 40 nsec electron beam from a Febetron, OH, HO_2 , NH_2 , NH, and ClO have been produced and their participation in more than 40 reactions of importance has been investigated in combustion and pollution chemistry, including reactions with aromatics which will be present in sizable quantities in synthetically derived fuels.

ARGONNE NATIONAL LABORATORY
Chemistry Division (Continued)

26. RESEARCH IN COMBUSTION FUELS \$280,000 01-1
 M. S. Matheson, S. Gordon, L. Kaplan,
 M. C. Sauer, J. R. Miller

Radiation and photochemical techniques are used to study reactions of interest in the processing of combustible fuels. Two areas being investigated are: (1) reactions of coal model compounds, and (2) direct reaction of water with carbon to produce hydrogen. Since gasification and liquefaction of coal are free radical processes, reactions are studied of coal model compounds with radiation chemically produced free radicals. In particular, reactions are studied which can lead to elimination of organically bound sulfur and those which split the aliphatic and heteroatom bridges linking the aromatic structures in coal. Kinetics and intermediates are studied with pulse radiolysis, while final products are obtained by steady gamma radiolysis. Rates and intermediates for reactions of OH, O[•], e⁻ with benzo- and dibenzothiophene derivatives have been measured. Aspects of the water-gas reaction are being examined using a focused laser to drive the carbon-water reaction which generates H₂, CO and CO₂, depending on temperature and other conditions.

27. CHEMICAL AND PHYSICAL \$377,000 01-1
 PROPERTIES OF CHLOROPHYLL
 J. J. Katz, J. R. Norris, L. L. Shipman,
 M. R. Wasielewski, M. K. Bowman,
 J. C. Hindman, H. L. Crespi

This research strives to attain a detailed understanding of the chemical and physical properties of chlorophyll as an absolute essential to the interpretation of chlorophyll function in photosynthesis on the molecular level. Heavy emphasis is placed upon the use of magnetic resonance, infrared (ir) and visible absorption spectroscopy and, most recently, photo-electron and fluorescence spectroscopy and small angle neutron scattering (SANS). Recent discovery of the laser properties of chlorophyll has generated new studies of the excited states of chlorophyll from their lasing characteristics. The electronic properties of chlorophyll are also studied in a theoretical effort which includes ab initio all-electron calculations, and applications of exciton and Förster theory to energy transfer in chlorophyll.

ARGONNE NATIONAL LABORATORY
Chemistry Division (Continued)

28. PHOTOSYNTHESIS STUDIES: \$182,000 01-1
REACTION CENTER STRUCTURE
AND FUNCTION AND ASSOCIATED
ELECTRON TRANSFER EVENTS
J. R. Norris, M. C. Thurnauer, M. K. Bowman

The objective of this research is to acquire information on the structural details of in vivo photosynthetic reaction centers, particularly those relating to the orientation and distances between the electron transfer agents involved in chlorophyll special pair function. Electron spin echo (ESE) spectroscopy is being developed as a tool of altogether unusual power and sensitivity for photosynthesis studies. ESE, EPR, and related optical studies (fluorescence, photo-bleaching, optical transients) are being used: (1) to investigate the orientation of the two chlorophylls in the special pair relative to each other; (2) to deduce the spatial relationships of electron transfer agents relative to the special pair; (3) for a global survey of photo-reaction centers to determine whether there is a range of chlorophyll special pair structures, and what that range may be; (4) for application to other problems in photosynthesis such as oxygen evolution in green plants.

29. ARTIFICIAL PHOTOSYNTHESIS \$209,000 01-1
M. R. Wasielewski, W. Svec, J. J. Katz

The objective of this research is to develop solar energy conversion systems that mimic the way photosynthetic organisms use light for chemical purposes. There are four major components in this research effort: (1) synthesis of photo-active chlorophyll special pairs, analogs, and derivatives of improved stability and operating characteristics; (2) electrochemical investigations of electron transfer and the mechanism of charge transfer in synthetic reaction centers; (3) biomimetic devices for solar energy conversion using synthetic photo-reaction centers; (4) a molecular electronics program to develop efficient electron-transport chains required for efficient operation of a biomimetic solar energy conversion device.

ARGONNE NATIONAL LABORATORY
Chemistry Division (Continued)

30. PREPARATION OF ORGANISMS AND BIOLOGICAL MATERIALS OF UNUSUAL ISOTOPIC COMPOSITION \$172,000 01-1
J. J. Katz, H. L. Crespi, M. R. Wasielewski

A principal objective of this project is the large-scale cultivation of organisms in which the usual isotopes ^1H , ^{12}C , ^{14}N , ^{24}Mg are essentially completely replaced by the rare heavy stable isotopes ^2H , ^{13}C , ^{15}N and ^{25}Mg . These organisms find many important applications in magnetic resonance and spectroscopic research. Organisms such as fully deuterated algae are also used as a source of deuterated photosynthetic pigments, proteins, lipids, chloroplasts, chromatophores, and reaction centers, which find a multitude of uses in photosynthesis research. Associated with the preparative work is a limited effort for the isolation of chlorophyll-protein complexes and the development of new methods for preparing reaction centers. Another important component of this project is the routine preparation of the large amounts of photosynthetic pigments of ordinary isotopic composition required for a number of research activities.

31. THEORETICAL CHEMISTRY AND MODELING \$312,000 01-2
T. H. Dunning, Jr., P. A. Benioff,
G. Das, A. F. Wagner

The recently reorganized theoretical chemistry research consists of studies of the basic mechanisms of combustion processes, atmospheric pollutants arising from combustion processes, gas-solid interactions applied to high-temperature and sputtering processes, fundamental molecular-beam interactions, potential energy curves and spectra of diatomic molecules, and quantum chemistry code development. The basic thrust of this work is the ab initio calculation of molecular electronic structure and spectra, interatomic and intermolecular potential energy curves and surfaces, and chemical dynamics on those curves and surfaces. Capabilities include both rigorous, highly accurate techniques applicable to small systems and approximate, inexpensive techniques applicable to large molecules or large clusters of small molecules.

ARGONNE NATIONAL LABORATORY
Chemistry Division (Continued)

32. HIGH RESOLUTION SPECTROSCOPY \$240,000 01-2
H. M. Crosswhite, F. S. Tomkins, K. T. Lu

Spectroscopic properties of states having large principal quantum numbers near the ionization threshold are being studied for a series of elements beginning with barium (a two-electron system) and several representative lanthanides, then ultimately including the actinides uranium through americium. Pulsed dye laser absorption spectroscopy of selected excited states is used to isolate their Zeeman behavior, and an analysis of diamagnetic interactions in terms of configuration-mixing and photoionization phenomena is made by the use of Multichannel Quantum Defect Theory. Quantitative measurements of transition probabilities for atomic vapors are in progress for uranium through americium, using the differential-interferometer "hook" method. Spectroscopic analyses of the energy levels of neutral and singly-ionized actinides uranium through einsteinium will be brought to a conclusion. This will include development of a parametric model of atomic electron and hyperfine interactions applicable to all lanthanide and actinide cases, including properties of ions in metals and optical crystals.

33. CROSSED-BEAM REACTION STUDIES \$203,000 01-2
OF ACCELERATED ATOMS AND
MOLECULES
S. Wexler, E. K. Parks, C. E. Young

Mechanisms, cross sections, energetics and dynamics of chemi-ionization reactions are studied experimentally by crossed-molecular beam methods and by statistical and semi-classical scattering theory. Classes of reactions under investigation are associative ionization, rearrangement ionization, electron transfer and collision-induced dissociation to pairs. Studies include chemi-ionization reactions of ground state and laser-excited actinide (U, Th) and lanthanide (Ce, La) metal atoms with O₂, collision-induced dissociation of alkali halides, electron transfer of ground state and excited alkali atoms with O₂ and metal hexafluorides with high electron affinities, and associative ionization combustion reactions of free radicals.

ARGONNE NATIONAL LABORATORY
Chemistry Division (Continued)

34. MOLECULAR SPECTROSCOPY \$143,000 01-2
J. R. Ferraro, L. J. Basile

Molecular spectroscopy applied to the determination of the molecular structure of different phases produced by temperature and/or pressure changes. Synthesis and study of new ionic, semi-, super-, and one-dimensional electrical conductors. Development of new thermochromic compounds, some with possible device applications, e.g., window coatings. Theoretical calculations (normal coordinate analyses) for molecular structure verification.

35. CHEMISTRY OF THE MHD PROCESS \$102,000 01-2
J. C. Hindman

This experimental-theoretical study was initiated in FY 1978 to gain an understanding of the factors which control plasma conductivities in coal-fired MHD generators. The experimental research involves kinetic studies of electron production from seed materials, e.g. K_2CO_3 , and studies of electron scavenger reactions in flames, a plasma torch and eventually in the ANL MHD test generator. Theoretical studies involve complementary modeling studies and quantum chemical calculations of the properties of molecules and radicals in hot plasmas. These latter calculations include predictions of dipole moments and electron affinities for the species present.

36. ELECTRON SCATTERING CROSS \$ 9,000 01-2
SECTIONS GOVERNING THE
ELECTRICAL CONDUCTIVITY OF
COAL-FIRED MHD PLASMAS
M. Inokuti

The efficiency of an open-cycle, coal-fired MHD generator is proportional to the electrical conductivity of its working fluid, i.e., a partially ionized gas containing many high-temperature molecular species. The conductivity, in turn, is determined by the cross sections for low-energy (<10 eV), electron collisions with those molecular species. The present work aims at providing theoretical and experimental cross-section data that is crucial for sound modeling of plasma properties necessary for the optimization of the MHD generator, with respect to maximizing the efficiency and minimizing toxic effluents.

ARGONNE NATIONAL LABORATORY
Chemistry Division

37. THE CHEMICAL NATURE OF COALS \$245,000 02-1
AND COAL PRODUCTS
M. H. Studier, R. Hayatsu, R. E. Winans,
R. G. Scott, R. L. McBeth, L. P. Moore

Investigation of logical diagenesis: biological materials - peat - lignite - sub-bituminous - bituminous - anthracite. Correlation with chemical structures of petroleum, shale oil, Fischer-Tropsch products, for contribution to coal conversions. Vacuum-distillation and solvent-extraction isolation of trapped compounds in coals for clues to the formation and nature of the coal. Pyrolysis, hydrocracking and oxidative degradation to produce identifiable compounds; isolation and identification by fractional distillation, chromatography and mass spectrometry.

38. INORGANIC CHEMISTRY \$265,000 02-1
E. H. Appelman, J. G. Malm, L. Stein

The chemistry of fluorine and highly reactive fluorides as well as the chemistry and applications of unusual oxidizing agents is emphasized. Support is given to the solution of chemical problems arising in the chemi-ionization process of uranium isotope separation now under development at ANL. Methods are under development to collect radon, xenon and, perhaps, krypton by chemical means on solid absorbers. Extensive studies are being conducted on the newly discovered stable dioxenon cation, Xe_2^+ , in solution. Reactions between unusual oxidants and fluorinating agents developed at ANL (e.g., noble gas compounds, perbromates and hypofluorous acid) and a variety of organic and inorganic compounds are being studied.

ARGONNE NATIONAL LABORATORY
Chemistry Division (Continued)

41. ANALYTICAL DEVELOPMENTS IN MASS SPECTROMETRY-CHROMATOGRAPHY AND SUPPORTING SYSTEMS \$145,000 02-3
M. H. Studier, R. Hayatsu, R. E. Winans,
R. G. Scott, R. L. McBeth, L. P. Moore

The emphasis is on the improvement of instruments, procedures and data handling systems. Time-of-flight mass spectrometers in combination with chromatographic and high-vacuum techniques of separation are used primarily to identify the macro-molecular components and structure of fossil fuels and their conversion products, and also as an analytical support facility for other programs such as chlorophyll-photosynthesis, catalyst, and superconductor research.

42. STUDY OF ATMOSPHERIC TRACE GASES BY MASS SPECTROMETRY \$131,000 02-3
C. M. Stevens, R. Gorse, E. H. Appelman

Atmospheric processes are being studied by use of isotopic labeling techniques and high-resolution, high-sensitivity mass spectrometry. The atmospheric CO cycle is being studied to determine its sources and production rates, as well as average atmospheric concentrations of photochemically produced OH radical. Analytical methods are being developed to directly measure the atmospheric concentration of OH by reaction with $^{13}\text{CH}_2\text{O}$ to form ^{13}CO , followed by mass spectrometric analysis. C_2D_6 is being tested as a continental and global scale tracer for atmospheric transport and dispersion studies.

43. RADIOACTIVE ISOTOPES AND NUCLEAR TECHNIQUES AS ANALYTICAL TOOLS FOR BIOLOGICAL PROBLEMS \$ 24,000 02-3
A. M. Friedman

Development of nuclear analytical techniques to study a number of different biological processes. Investigation of the mechanism of sulfur uptake into peat to understand the pathway for incorporation of sulfur into coal and, thereby, gain possible insight into sulfur removal from coal. Development of methods to synthesize γ -amino butyric acid analogs tagged with radioactive halogens to measure turnover rates of important neurological transmitters.

ARGONNE NATIONAL LABORATORY
Chemical Engineering Division

F. A. Cafasso - Phone: (FTS) 972-4542 or (312) 972-4542

44. FLUID CATALYSIS \$140,000 02-1
H. M. Feder, F. A. Cafasso

This research has two major components. The first involves critical tests of reaction catalysis in a fluid stream by a suspension of immiscible liquid droplets; study of reversible reactions to transfer a homogeneous catalyst from a carrier phase to a working phase (partition catalysis); formation of a surface-active catalyst at the interfacial film between the carrier and working phases (surfactant catalysis); investigation of hydrogenation of aromatic molecules and valence isomerization of highly-strained molecules; and comparison of homogeneous and two-phase systems using a well understood test reaction. The second involves new homogeneous, catalytic reactions which produce alcohols and their formate esters from synthesis gas; mechanism of the reactions; optimization of rate and selectivity for desirable products; research on Fischer-Tropsch analogues; and extension of hydrogen atom transfer-radical pair mechanism to reduction of CO_2 .

ARGONNE NATIONAL LABORATORY
Physics Division (Continued)

47. LASER AND RF SPECTROSCOPY OF FREE ATOMS AND MOLECULES
L. Goodman, W. C. Childs
- \$188,000
- 01-3

This research uses laser and radiofrequency techniques to study in detail the structure of free atoms and molecules, much of the work involving actinide atoms or molecules containing them. The project also supports theoretical work designed to better understand atomic and molecular structure treating such aspects as core polarization, Sternheimer shielding and the use of effective operators in hyperfine interactions. More specifically, the theoretical work is being developed to explain the observation of an isotope shift that depends upon the vibrational motion coupling to electronic transitions. These shifts are being observed using single-frequency tunable dye lasers, in particular employing the intracavity laser-quenching technique, and the Argonne 30-foot grating spectrograph. The hyperfine structure information is also obtained using Doppler-free laser spectroscopy and present experiments involve identification of the ground and low-lying excited states of ^{221}Fr derived from the decay of ^{229}Th .

48. MÖSSBAUER EFFECT RESEARCH
G. J. Perlow
- \$ 72,000
- 01-3

Exploration of new and potentially important extensions of the Mössbauer effect. Experiments with narrow resonances; ^{67}Zn , experiments on relativistic and other small effects in solids; ^{181}Ta . Radiofrequency techniques in Mössbauer spectroscopy; to obtain precise hyperfine measurements, to produce short time-burst of gamma rays, and to study the generation of delayed ultrasound in low-temperature metals. Studies of specialized solids; intercalation compounds of graphite, in particular compounds of cesium with graphite, and the products by intercalation of xenon fluorides in graphite.

ARGONNE NATIONAL LABORATORY
Physics Division

49. BEAM FOIL RESEARCH AND COLLISION DYNAMICS OF HEAVY IONS
 H. G. Berry \$223,000 01-3

Processes involving energetic (MeV energy) and multiply-ionized heavy ions; their atomic parameters such as energy levels and radiative lifetimes; their production, de-excitation and re-excitation by collisions in passage through gases and solids and at surfaces. Systematic variation in energy of x-ray resonance radiation and fluorescence at lower energies in the vacuum ultraviolet region; decay channels of excited, multiply-ionized atoms most easily detectable and distinguishable from those of other species. Measurements of picosecond lifetimes. Approaches to quasi-equilibrium of fast moving ions through matter; analysis in terms of the radiation from excitation states of the associated clouds of electrons. Strong surface effects on electronic angular distributions (orientation and alignment). Lamb shifts and fine structure of 2- and 3-electron ions.

50. MONOCHROMATIC X-RAY BEAM PROJECT
 S. L. Ruby \$109,000 01-3

Production of intense monochromatic x-ray beams by Bragg reflection of synchrotron radiation from crystals containing Mössbauer-resonant nuclei. The initial goal is to produce reflected beams having angular divergence less than 10^{-8} steradian and coherence length around 10 meters.

51. DISSOCIATION AND OTHER INTERACTIONS OF ENERGETIC MOLECULAR IONS IN SOLID AND GASEOUS TARGETS
 D. S. Gemmell \$309,000 01-3

Interactions of fast (0.3 to 4.0 MeV) molecular ions (H_2^+ , H_3^+ , HeH^+ , OH^+ , N_2^+ , etc.) with matter, 4-MV Dynamitron. Joint energy-angle distributions with high resolution ($\sim 0.005^\circ$ and ~ 250 eV) for the breakup fragments arising when such beams bombard thin (~ 100 Å) foils. Interaction between the projectiles and the polarization oscillations induced in the target foil. Transmission of molecular ions through foils. Effective charge states of ions inside matter. Determinations of structure for the incident molecular ions.

ARGONNE NATIONAL LABORATORY
Physics Division (Continued)

<u>52.</u>	CHARGE-EXCHANGE CROSS	\$ 35,000	01-3
	SECTION CALCULATIONS FOR		
	HEAVY-ION-INITIATED INERTIAL		
	CONFINEMENT FUSION		
	Y.-K. Kim, G. Das		

Calculations of charge transfer cross sections needed for the design of accelerators for heavy-ion-induced inertial confinement fusion reactors. Ion-ion collisions (between beam particles) and ion-background gas collisions.

BARTLESVILLE ENERGY TECHNOLOGY CENTER

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Bartlesville Energy Technology Center

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53. THERMODYNAMIC CHARACTERIZATION \$125,000 02-1
OF CONDENSED-RING COMPOUNDS
W. D. Good

Determination of thermodynamic properties for the major compound types present in syncrude from coal, shale oil, and heavy ends of petroleum. Selective studies on key condensed-ring aromatic and hydrosubstituted compounds are undertaken to form an adequate experimental base for broad-ranged correlating equations based on chemical structure. This 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.

BROOKHAVEN NATIONAL LABORATORY
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Chemistry Department

J. Hudis - Phone: (FTS) 666-4301 or (516) 345-4301

54. RADIATION CHEMISTRY \$463,000 01-1
B. H. J. Bielski, R. W. Dodson,
R. A. Holroyd, H. A. Schwarz

Behavior and reactions of transient chemical species (ions, electrons, free radicals, and excited states of molecules); theories to explain their behavior; development of new or improved techniques; radiolysis and photolysis to produce the transient species, usually by pulse techniques. Principal areas of investigation are: properties and reactions of electrons in dielectric fluids; reactions of superoxide radicals and singlet oxygen in biological systems; infrared spectra of protonated molecular clusters in gas phase; reactive metal ion intermediates in redox reactions.

55. CHEMISTRY OF ENERGETIC ATOMS \$619,000 01-1
WITH APPLICATIONS TO NUCLEAR
MEDICINE
G. Harbottle, R. M. Lambrecht,
A. P. Wolf

Chemistry of energy-rich atomic and molecular species, studies with neutral and charged reactants in either their ground or electronically excited states or as entities with high kinetic energies. Reactive intermediates produced by nuclear processes; carbon, nitrogen, oxygen, and halogen atoms both kinetically and electronically excited; probe details of atom-atom and atom-molecule reactions in an energy range inaccessible to conventional methods. Microwave plasma generation of atomic species provides the same atomic species in known electronic states and temperature distributions; spectroscopic techniques to identify reactants and products and to determine rates of gas phase reactions.

BROOKHAVEN NATIONAL LABORATORY
Chemistry Department (Continued)

56. ENERGY TRANSFER IN CHEMICAL KINETICS
R. E. Weston \$133,000 01-1

Collisional transfer of energy from electronically or vibrationally excited atoms or molecules; rate measurement by determination of fluorescence lifetime; competition between fluorescence and energy transfer rates; energy distribution in products as a probe of reaction mechanism; bimolecular rate constants and cross sections for energy transfer; direct lifetime measurements in 1-100 nsec range by time-correlated single photon counting.

57. PHOTOCHEMICAL ENERGY CONVERSION AND SOLUTION KINETICS
C. Creutz, N. Sutin \$359,000 01-1

Transition metal complexes as mediators in solar energy conversion and storage; photochemical investigations of such complexes and elucidation of the electron-transfer properties of charge-transfer and ligand-field excited states through studies of their reactions with inorganic oxidants and reductants in solution. Decomposition of water into hydrogen and oxygen. Quantitative study of the physical and chemical deactivation processes such as luminescence, radiationless decay, and chemical "back-reactions"; lifetimes and other physical properties of excited states; rates of thermal electron-transfer reactions of transition metal complexes.

58. SELECTIVE LASER-INDUCED CHEMISTRY
D. Brenner \$ 86,000 01-1

Selective laser-induced chemistry; chemistry of excited-state molecules; criteria for selectivity in photochemical reactions involving specific bond cleavages or isotope enrichments. Reactions of vibrationally excited molecules; rate of intramolecular energy flow among the vibrational modes; V-V and V-T/R energy transfer; intramolecular chemical dynamics after the absorption of a photon in the absence of collisions. Excess energy of reactions in exothermic processes, i.e., how is the exothermicity partitioned among products and to what extent is the energy distribution statistical; measurement of transfer of energy from visible and UV photons to photochemical products. Laser-induced fluorescence for measuring internal energy distributions, arrested relaxation and isotope separation for examining mode specific phenomena, photodissociation in molecular beams.

BROOKHAVEN NATIONAL LABORATORY
Chemistry Department (Continued)

62. ION-MOLECULE REACTIONS WITH APPLICATIONS TO FUSION ENERGY SYSTEMS \$330,000 01-2
R. Beuhler, L. Friedman

Mechanisms of evaporation of large molecular systems from rapidly heated solid surfaces, energy transfer in such processes and energy transfer in the collisions of molecular ions with solid surfaces; development of mass spectrometric techniques for identification and structural analysis of large fragile molecular systems; auxiliary pigment responsible for the absorption of radiant energy in the photosynthetic processes in blue-green algae. Nondestructive evaporation, gentle ionization, and highly sensitive detection for the characterization of these compounds by mass spectrometric techniques. Evaporation mechanisms in systems suddenly heated to high temperatures relevant to attempts to develop controlled thermonuclear reactions; very intense sources of highly charged macromolecular weight ions; rapidly produced phase transitions. Detection of molecular aggregates and methods of determination of their charge as well as their mass to charge ratio; individual singly ionized particles that have molecular weight in excess of a few thousand; development of techniques for the sensitive detection of very heavy energetic ions.

63. MOLECULAR BEAM STUDIES OF CHEMICAL DYNAMICS USING SHORT-LIVED RADIOACTIVITY AND SYNCHROTRON LIGHT \$220,000 01-2
J. R. Grover

Crossed molecular beam technique in which one of the reagent beams is labeled with short-lived ($\leq 10^{-1}$ sec) radioactive isotope; detection of radioactive disintegrations; absolute differential cross sections for reactive scattering with a sensitivity ten times that obtained in other crossed beam experiments. Prototype experiments on $\text{HAt} + \text{Cl}$, $\text{Br} \rightarrow \text{At} + \text{HCl}$, HBr ; ^{217}At , $t_{1/2} = 0.032$ sec; extension of the technique to accelerator-produced isotopes where results to date make it reasonable to expect that cross sections as small as 10^{-5} Å² can be subjected to differential study. Experimental determinations of reactive potential hypersurfaces to test and calibrate semi-empirical theories now under development.

BROOKHAVEN NATIONAL LABORATORY
Chemistry Department (Continued)

64. NEUTRON SCATTERING STUDIES \$500,000 01-2
 L. M. Corliss, J. M. Hastings

Measurement of the energy and momentum changes undergone by neutrons scattered by a solid to obtain the complete space-time correlation function of the solid, from which, in principle, all its structural and dynamic properties can be obtained.

65. STRUCTURE AND BONDING IN \$250,000 02-1
 METAL HYDROGEN SYSTEMS:
 ESCA, EXAFS, DIFFRACTION
 STUDIES
 J. Hudis, M. L. Perlman,
 T. F. Koetzle

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

66. MECHANISMS OF PHOTO-, \$180,000 02-1
 ENZYME-, AND CHEMICALLY
 CATALYZED CIS-TRANS
 ISOMERIZATION AND
 APPLICATIONS TO ENERGY
 STORAGE
 S. Seltzer

Mechanisms of photo-, enzyme-, and chemically-catalyzed cis-trans isomerization and how they can be utilized to maximize the energy difference between photostationary and thermodynamic equilibrium states; study of a synthetic photogalvanic cell utilizing the photoisomerization of fumaric to maleic acid.

BROOKHAVEN NATIONAL LABORATORY
Department of Energy and Environment

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D. H. Gurinsky - Phone: (FTS) 666-3504 or (516) 345-3504
D. J. Metz - Phone: (FTS) 666-3054 or (516) 345-3054

69. INVESTIGATION OF THE CHEMISTRY OF ENERGETIC COMPOUNDS \$170,000 01-1
M. Hillman

Preparation, structure, and chemistry of energetic compounds; possibilities of both photoconductivity and superconductivity in organic molecules; preparation of three-dimensional organic arrays that are potential conductors; photoconductivity studies of intensely colored derivatives of compounds that are already known to have some conductivity properties; ferrocene.

70. KINETICS AND MECHANISMS OF CHEMICAL PROCESSES RELATED TO THE DEVELOPMENT AND USE OF ENERGY \$160,000 01-1
J. W. Sutherland

Basic kinetic and mechanistic details in specific chemical systems for which present data are inadequate or unavailable; input data for energy models. Flash photolytic and pulse radiolytic techniques to characterize short-lived transient chemical species; steady-state photolytic, steady-state radiolytic, and standard kinetic techniques to identify and measure yields of final products of a particular overall reaction. Chemical reactivity of sulphur dioxide in aqueous solution, chemistry of transient intermediate nitrogen-hydrogen compounds, and photochemistry in the adsorbed state.

BROOKHAVEN NATIONAL LABORATORY
Department of Energy and Environment (Continued)

75. HIGH TEMPERATURE CHEMISTRY \$175,000 02-1
 J. J. Egan

This project studies the thermodynamic and transport properties of substances at high temperatures and attempts to explain the results in terms of appropriate atomic models. Electrochemical methods are stressed since they yield very accurate results and also have possible direct application to batteries, fuel cells, and solar cells, when new methods are developed. The techniques of solid state electrochemistry are studied extensively and work is directed toward development of this relatively new field. The movement of electrons and electron holes in both ionic crystals and molten salts is being examined in view of its fundamental importance and its potential applications. Substances of interest include alloys that are semiconductors in the liquid and solid state with applications to solar cells, solid and molten salt electrolytes with direct application to high energy batteries and fuel cells, as well as high temperature reactor fuels.

76. CHEMISTRY AND PHYSICS OF \$210,000 02-1
 COAL UTILIZATION
 R. T. Yang, D. R. Mackenzie

The objective of this study is to understand the fundamental reactions occurring in several coal conversion and utilization processes. Processes of interest include combustion, gasification, liquefaction, desulfurization, and carbonization, and work proceeds along three main lines of investigation: (1) high temperature (800-1600 C) gas-carbonaceous material reactions; (2) mechanisms of hydrogenation; and (3) mechanically assisted hydrogenation (mechanochemistry), a phenomenon recently observed in the course of these studies.

BROOKHAVEN NATIONAL LABORATORY
Department of Energy and Environment (Continued)

77. METAL HYDRIDES \$275,000 02-1
R. H. Wiswall, J. J. Reilly

Elucidation of the thermodynamic and structural principles and behavior of metal-hydrogen systems; pressure-temperature-composition relationships; hydrogen isotope exchange between hydride and gas phases; x-ray and neutron diffraction measurements of the crystal structure and state of the hydrogen atom; methods for and synthesis of metal hydride single crystals; impact on energy storage, energy conversion, and isotope separation.

78. CYCLIC SEPARATIONS PROCESS \$140,000 02-2
RESEARCH
F. B. Hill

Application of cyclic processes to separations of interest in energy technology; heatless fractionation, parametric pumping, cycling zone adsorption, and preparative chromatography; experimental investigations of protium-tritium separation by pressure and temperature cycling processes using the hydrogen-vanadium hydride system; equilibrium and kinetic measurements; theoretical models to predict process performance. Process design studies; measurement of fluid-solid separation systems.

79. DETERMINING FRAGILE MOLECULES \$110,000 02-3
IN THE ENVIRONMENT
L. Newman, R. Tanner

The long term goals of this research 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-specific element detection techniques. Since many substances of interest may be reactive under analysis conditions, 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. Potentially applicable to dynamically varying concentrations of (aqueous) ammonium, phosphate, nitrate, weak organic acids, (atmospheric) ammonia, nitric acid, particulate sulfates, nitrates, in the environment.

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Chemical Biodynamics Division

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82. PHOTOSYNTHETIC SOLAR ENERGY \$330,000 01-1
UTILIZATION
J. Otvos, M. Calvin

This research is predominantly a basic science effort and is directed towards developing methods, based on research in green plant photosynthesis, for the utilization of solar energy. It includes studies in three distinct areas: (1) Photosensitized electron transfer reactions: This research involves synthesis of surfactant sensitizers, such as porphyrins and various transition metal complexes with alkyl chains attached, selection and characterization of interfacial systems to serve as vehicles for the electron transfer reaction, and photochemical studies on the substrate reactants. The synthetic work is well along and has supplied many surfactant dyes that are now being used. Interfacial systems include polymeric latex suspensions for studying surface electron transfer by fluorescence techniques, and both phospholipid vesicles and microemulsions for searching for photosensitized electron transfer from one compartment to another across an interfacial layer. (2) Sensitized photovoltaic devices: This work continues with small band gap semiconductors. Development of a novel dry, dye-sensitized Schottky barrier solar cell is being pursued. After learning how to optimize the various layer thicknesses it should be possible to produce these cells with polycrystalline materials easy to fabricate. (3) Hydrocarbons and energy from plants: The species Euphorbia lathyris continues to be analyzed for composition of its latex. Optimized procedures for extraction of the latex components from the whole plant are being developed and chemical processing of the extract that would make it suitable as a liquid fuel is being explored.

LAWRENCE BERKELEY LABORATORY

Energy and Environment Division

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83. PHOTOCHEMICAL CONVERSION OF SOLAR ENERGY UTILIZATION
L. Packer

\$125,000

01-1

The research mainly involves: Studies of the molecular mechanism of H⁺ translocation by bacteriorhodopsin; studies of membrane channels and ionophores from related biological energy transducers and in fragments of bacteriorhodopsin to develop a simpler system for H⁺ translocation; construction of a photovoltaic cell derived from bacteriorhodopsin and planar millipore-filter stabilized membranes, including orientation of the catalyst within the structure of the photocell and studies of factors affecting the stability during illumination; applications of the photocell to develop laboratory scale solar power cells, desalination and concentration cells.

84. UNIMOLECULAR STUDY OF DISSOCIATION AND RECOMBINATION REACTIONS
N. Brown

\$ 20,000

01-2

This work has five objectives: (1) to improve the theoretical description of the collisional intermolecular energy transfer process which is rate controlling at low pressures, (2) to apply the formalism developed in (1) to reactions of importance in combustion processes, (3) to improve the description of the limiting high pressure kinetics, (4) to apply the formalism developed in (3), to determine rate data for reactions of importance in combustion, and (5) to extend rate data between the low and high pressure limits using the method of reduced fall off.

85. SELECTIVE HYDROGENATION OF COAL
E. A Grens, T. Vermeulen

\$195,000

02-1

The areas of investigation that are being pursued in this continuing project for the development of the basis for conversion of coal to liquids below coal pyrolysis temperature include: interaction breaking of certain bond types in the coal structure with the use of homogeneous catalysts; interaction of coals with inorganic and organic reaction media; action of catalyst materials on specific bond types in model compounds at moderate temperatures; use of mixed inorganic/organic media for coal liquefaction; catalytic removal of organic sulfur and nitrogen.

LAWRENCE BERKELEY LABORATORY

Materials and Molecular Research Division (Continued)

91. ENERGY TRANSFER AND STRUCTURAL \$140,000 01-2
STUDIES OF MOLECULES ON SURFACES
C. B. Harris

Studies in the visible and ultraviolet have shown major changes in the interactions, bonding and chemical reactivity of various small oxidizing molecules on single crystal nickel (111) surfaces. The studies have included O_2 , NO, and most importantly NO_2 , a major constituent of smog and atmospheric systems, and an important molecule in metallic corrosion and oxidation. In order to accomplish these experiments an ultra high vacuum system to do optical spectroscopy of molecules on metal surfaces in the UV and visible region of the spectrum has been constructed. It can investigate the optical properties of single crystal metal surfaces and adlayers over the temperature range $10^\circ K$ to $400^\circ K$. The idea underlying these experiments is quite simple. When a monolayer or thin film of these materials is deposited on a cold nickel surface at approximately $20^\circ K$ the optical properties of the adsorbed monolayer reflect the physi-adsorbed state since little reaction occurs at these temperatures upon deposition. Upon warming, however, one can spectroscopically detect and follow the transition between the physi-adsorption and chemi-adsorbed phase. Since one can simultaneously monitor temperature with changes in the optical properties of the surface one is able to get the activation energy for the reaction directly at the surface. The sensitivity of the system is such that a change in surface optical parameter when as little as 0.5% coverage of an adlayer is deposited is readily discernable. In addition, the optical spectroscopy and cracking patterns of larger organic molecules on single crystal surfaces have been investigated. The optical spectra of pyrazene at a coverage of approximately $1/3$ a monolayer on Ni (111) shows both the $n\pi$ and the $\pi\pi$ transitions. They are clear at $10^\circ K$ but upon warming from 20° to $100^\circ K$ the intensities change and new peaks which are related to the products in the reactive channel appear. The fragmentation pattern at room temperature from quadrupole masspec has been assigned to $CN + H_3C_3N$. Finally the widths of the optical transitions as a function of temperature can be determined. This provides valuable information about the energy transfer mechanisms from the organic into the metal as a function of temperature.

LAWRENCE BERKELEY LABORATORY
Materials and Molecular Research Division (Continued)

92. PHYSICAL CHEMISTRY WITH EMPHASIS \$ 85,000 01-2
ON THERMODYNAMIC PROPERTIES
K. S. Pitzer

Thermodynamic properties of aqueous electrolytes to treat very complex solutions at room temperature and at high temperatures and pressures where such solutions appear in many practically important processes including those related to geothermal energy. Construction and use of a calorimeter measuring heat capacity up to about 300°C and a kilobar and the development and use of improved equations based on statistical mechanics to allow prediction of properties at temperatures and compositions other than those measured. Development of a quantum chemistry for heavy atoms where relativistic effects are important, prediction of numerous properties of molecules containing heavy atoms; effective potentials for valence electrons, with the relativistic effects included in these potentials.

93. CHEMICAL DYNAMICS STUDIES \$170,000 01-2
B. H. Mahan

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 induced fluorescence has been constructed and operated successfully.

LAWRENCE BERKELEY LABORATORY

Materials and Molecular Research Division (Continued)

94. THEORY OF ATOMIC AND MOLECULAR COLLISION PROCESSES \$ 75,000 01-2
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.

95. PHOTOELECTRON SPECTROSCOPY \$650,000 01-2
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.

LAWRENCE BERKELEY LABORATORY

Materials and Molecular Research Division (Continued)

102. CONVERSION OF COAL TO CLEAN LIQUID AND GASEOUS FUELS
G. A. Somorjai, A. Bell

\$165,000

02-1

Development of catalytic approaches for the conversion of coal to liquid and gaseous fuels; catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen produced by coal gasification; factors which limit catalyst activity, selectivity, and resistance to poisoning; relationship between catalyst composition/structure and performance; synthesis and evaluation of novel homogeneous catalysts based upon mono- and polynuclear organometallic complexes for coal liquefaction; emphasis on developing catalysts to complex aromatic groups and selectively promote reactions with portions of aromatic substrates; elucidation of reaction pathways in the liquefaction of coal catalyzed by strong Lewis acids.

103. FORMATION OF OXYACIDS OF SULFUR FROM SO₂
R. E. Connick

\$ 65,000

02-1

Basic chemistry of sulfur dioxide, particularly in solution, and also the chemistry of the numerous sulfur-containing compounds formed in aqueous solutions of sulfur dioxide through reaction with bases and acids and through oxidation and reduction reactions, particularly with oxygen; spectrophotometric, Raman and NMR measurements.

104. ELECTROCHEMICAL SYSTEMS
J. Newman

\$ 50,000

02-1

Investigation of fluid flow and electrochemical transport; transport property measurements of concentrated electrolytic solutions; analysis of mass-transfer rates and current distribution; design methods of practical electrochemical systems; impact on local and overall corrosion rates. Analysis of interacting kinetic, mass transfer, and fluid flow phenomena for semiconductor electrode systems; impact on advanced solar energy conversion systems. Configuration of liquid junction cells with polycrystalline semiconductor electrodes.

LAWRENCE BERKELEY LABORATORY
Materials and Molecular Research Division (Continued)

105. HIGH ENERGY OXIDIZERS AND DELOCALIZED-ELECTRON SOLIDS \$110,000 02-1
 N. Bartlett

This research project exploits oxidizers which are the most oxidatively aggressive of known substances. The present concern is with two dimensional electrical conductors derived from graphite or layer boron nitride. Strong oxidizers such as the heavy metal hexafluorides and dioxygenyl salts, e.g. O_2AsF_6 , are being explored as a means of providing well ordered single crystal salts, of the type C_xMF_6 , for structural study and correlating physical behavior with bonding interactions. The use of graphite salts of the anions AsF_6^- , SbF_6^- , PtF_6^- and AuF_6^- as anodes to generate unknown species by carrying out anodic oxidation from melts is being investigated. Graphite salts which differ in stoichiometry by hydrogen alone [e.g. $C_{24}(SO_3F)_2 \cdot HSO_3F$ and $C_{24}(SO_3F)_3 \cdot 2HSO_3F$] are being sought as possible electrical energy storage systems and materials with high proton conduction capabilities.

106. SYNTHETIC AND PHYSICAL CHEMISTRY \$ 65,000 02-1
 W. L. Jolly

By means of x-ray photoelectron spectroscopy, atomic core electron binding energies are measured for a wide variety of inorganic and organometallic compounds. These energies are interpreted in terms of atomic charges and indicate the nature of the electron distribution and bonding in the molecules. By the interpretation of suitably measured core binding energies, it is possible to determine the extent to which transition metal d electrons engage in "back-bonding" in organometallic compounds, metal carbonyls and nitrosyls, etc. One can identify and distinguish various modes of ligand-metal bonding which have analogs in the molecules chemisorbed on metal surfaces and in the intermediates of catalyzed organic reactions. Core electron binding energies are also being used to calculate the energies of ordinary chemical reactions - such as reactions involving gas phase molecules and ions. Other work involves the synthesis and characterization of simple but novel compounds of the nonmetallic elements. Particular interest centers on compounds which can be used as reagents in a wide variety of syntheses or which can be used to form polymers or other useful materials.

LAWRENCE BERKELEY LABORATORY
Materials and Molecular Research Division (Continued)

109. MOLECULAR THERMODYNAMICS OF PHASE \$ 25,000 02-4
EQUILIBRIA FOR WATER-HYDROCARBON
SYSTEMS AT HIGH PRESSURES WITH
SPECIAL ATTENTION TO THE SYSTEM
BRINE-METHANE
J. Prausnitz

This research is concerned with experimental and theoretical work on water-hydrocarbon mixtures in the region 25-250°C and pressures to 2 kilobars. Molecular thermodynamic studies are being conducted on hydrocarbon-water mixtures at high pressures to provide macroscopic physico-chemical information on intermolecular forces, fluid structure and phase behavior in a system containing one nonpolar component and one polar, hydrogen-bonding component. The data for the water-hydrocarbon systems are being reduced and interpreted using a partition function recently developed by Beret and extended to mixtures by Donohue. This partition function is based on generalized van der Waals' theory: the free-volume term (repulsive forces) is given by the Carnahan-Starling equation for hard spheres and the potential-field term (attractive forces) is given by results of Alder using molecular dynamics for molecules obeying a square-well potential. Contributions from rotational and vibrational degrees of freedom are included in the partition function through a generalization of the Prigogine-Flory theory for polysegmented molecules. The ultimate goal of this research is to establish a computer program for calculating phase equilibria in hydrocarbon-water (or brine) systems at high pressure. The program will be based on a theoretical, molecular-thermodynamic framework with adjustable molecular parameters determined from selected experimental data.

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111. THERMOCHEMICAL PRODUCTION OF \$200,000 02-1
HYDROGEN FROM WATER
O. Krikorian

Exploration of the scientific feasibility of using closed-cycle thermochemical processes for producing hydrogen from water using nonhydrocarbon energy sources (nuclear, solar, etc.). The goals are: (1) to search for and develop new cycles that are viable cycles, (2) to improve known cycles through innovative chemical approaches, and (3) to conduct research on the mechanisms of complex reactions that are associated with thermochemical cycles and of general interest to process applications as well. Work related to the ZnSe cycle is being continued to establish its scientific and economic potential.

112. THE EFFECTS OF SURFACE IMPURITIES \$ 30,000 02-1
ON THE KINETICS OF FORMATION AND
DECOMPOSITION OF METAL HYDRIDES
R. Alire, S. Steward

Investigation of the effects of impurities on hydride surfaces and on the mechanisms and kinetics of hydride formation and decomposition by Auger electron spectroscopy, ESCA, scanning Auger microprobe and secondary ion mass spectroscopy.

LOS ALAMOS SCIENTIFIC LABORATORY

P Division

G. A. Keyworth - Phone: (FTS) 843-4117 or (505) 667-4117

115. RADIATION FROM HIGH TEMPERATURE \$ 70,000 01-3
PLASMAS SEEDED WITH HIGH-Z
ELEMENTS
L. A. Jones, D. B. Thomson

Ionization rates of multiply ionized (five to thirty times) species are being furnished in order to understand the behavior of impurity ions in current magnetic fusion plasma experiments and to estimate the radiative cooling and energy balance in future confinement devices. The extremely high temperature environment obtainable only at the LASL theta pinch is being used to determine the ionization rates of Li-like ions of nitrogen and oxygen, line identification and ionization rates for krypton IX-XII, and dielectronic recombination and the double excitation rates of neon IX. Time histories of successive ionization stages in the theta pinch seeded with the selected element are being compared to expected values in order to improve estimation procedures along isoelectronic sequences. Studies of the breakdown of high pressure gas when irradiated by a laser.

116. A STUDY OF ENERGY CONVERSION \$ 70,000 01-3
AND TRANSPORT IN SPACE PLASMAS
W. C. Feldman

This is an experimental and theoretical basic research investigation of plasma and ion physics of the solar wind, lower solar corona, and earth's bow shock. The aim of this research is to understand the nature, evolution and saturation mechanisms of heat flux, ion beam and thermal anisotropy driven instabilities in the solar wind. Satellite data are being used to yield information about the various sources of free energy in the particle velocity distributions in the solar wind and earth's bow shock. These data have been reduced to provide not only velocity moments of, but also two dimensional contours of the electron and the ion distribution functions. Simultaneous magnetic and electric field measurements are available and are being combined with particle data to yield a description of the interplanetary plasma at 1 A.U. that is far more complete than any other available. The heavy ion physics studies are also used to obtain an understanding of heat flow regulation and plasma acceleration mechanisms in critical regions close to the sun. One objective is to learn how random thermal and wave energy in the lower solar atmosphere is converted to directed kinetic energy of expansion to form the supersonic solar wind.

LOS ALAMOS SCIENTIFIC LABORATORY

Q Division

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117. VAPOR PHASE HEAT TRANSFER

\$ 60,000

01-3

W. A. Ranken, J. E. Kemme

The project objective is to develop working fluid and container combinations suitable for heat-pipe operation at temperatures between 600 and 900 K. The orientation is for heat-pipe applications in the area of industrial energy recovery and methanation of synthesis gas from coal that require long-life and trouble-free operation. Investigations are directed toward solving specific problems associated with readily available working fluids such as sulfur, mercury, and Dowtherm A. Various additives are being employed to lower the viscosity of sulfur and to promote wetting of heat-pipe wicks and containers with mercury. The effects of these additives are evaluated under actual operating conditions in a series of performance tests with each fluid. Tests also are conducted to establish the decomposition rate of fluids as a function of operating temperature. In these tests, variations of heat input rates and of initial purification procedures are investigated to establish how these factors affect thermal stability. The results should provide a sound basis for additional investigations of some organic fluids with potentially greater thermal stability. A variety of heat-pipe wick and container materials are employed with each fluid to establish combinations that are compatible and inexpensive.

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118. CHEMICAL KINETICS AND SURFACE CHEMISTRY
G. L. Karapinka

\$ 70,000

02-1

Determination of chemical reaction mechanisms and kinetics, and catalyst surface chemistry and activity during hydrodenitrogenation of model coal-derived organic nitrogen compounds, such as quinoline; comparison of catalysts such as cobalt molybdate on alumina, and transition metal organometallic compounds (molybdenum, iron, tungsten); determination of effect of valence state of metals (degree of reduction) on activity and selectivity for hydrogenation (insertion of hydrogen), hydrogenolysis (carbon-carbon bond cleavage), and hydrodenitrogenation (formation of ammonia); determination of back-reactions of ammonia; suggested applications to hydroliquefaction of coal, and catalytic hydrotreating of coal-derived liquid fuels.

MORGANTOWN ENERGY TECHNOLOGY CENTER

Analytical and Supporting Research DivisionW. E. Wallace, Jr. - Phone: (FTS) 923-7294 or (304) 599-7294

119. PARTICLE INTERACTIONS: SIZE \$ 52,000 02-2
DISTRIBUTIONS IN COMBUSTION
STREAMS
R. P. Treat

The general objective is to investigate the process of adhesion or coalescence of particles when they come in contact under conditions which are comparable to those found in the post combustion zone of a coal combustion stream. This process is significant in the evolution of the particles size spectrum. Studies are underway to investigate the coagulation of aerosols involving internal or external electromagnetic forces and the effect of the electromagnetic forces on the particle size distribution in combustion streams.

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120. FUNDAMENTAL INVESTIGATION OF METAL-HYDROGEN SYSTEMS \$200,000 02-1
 R. C. Bowman, Jr., G. C. Abell,
 M. P. Guse

Identification and evaluation of factors to permit improved metal hydride energy storage systems; Ti, V, Li, Mg, and transition metal systems. Determination of hydrogen transport mechanisms vs. crystal structure, composition, phase transformation; changing electronic structure vs. hydride formation; nature of metal-H bonds; effects of dopants. Hartree-Fock computer calculations of metals and metal-H clusters.

121. INVESTIGATION OF THE MECHANISMS OF THE REMOVAL OF RADIOACTIVE NUCLIDES FROM WASTE STREAMS \$ 75,000 02-2
 G. L. Silver

The objective of this investigation is to study the behavior of plutonium with inorganic compounds in order to: (1) determine solution conditions which influence the removal of plutonium from waste water by adsorption; (2) determine the chemical properties of adsorbents which influence this adsorption; and (3) illuminate the mechanism of waste water decontamination by adsorption processes. Several inorganic phosphorous compounds are being examined in this study. These phosphorous compounds have been selected because of their proven ability to remove ions from aqueous solutions or because they have properties which suggest the presence of this ability, and include such materials as zirconium phosphate, titanium phosphate, stannic vanadophosphate, commercial bone char, and metal phosphites such as $U(HPO_3)_2$. The ability of these compounds to remove plutonium from aqueous solution is studied as a function of solution pH, adsorbent composition, adsorbent capacity for plutonium, and plutonium valence state. Pentavalent neptunium is used to simulate pentavalent plutonium because theoretical calculations suggest pentavalent plutonium may play an unsuspected and important role in the chemistry of plutonium in mildly acidic, neutral, or mildly alkaline waste water. Two new and promising types of adsorbents for plutonium are being introduced; stannic vanadophosphate and an entire spectrum of metal phosphites not heretofore considered for purposes of waste water decontamination.

MOUND LABORATORY

Nuclear Operations Department (Continued)

122. ATOMIC AND MOLECULAR PROPERTIES \$240,000 02-2
AND THEIR RELATIONSHIP TO
SEPARATION PROCESSES
W. L. Taylor

Investigation of fundamental isotope properties for the improvement of isotope separation processes; experimental and theoretical work on gas transport and thermodynamic properties in solid, liquid, and gas phases; thermal diffusion factors by the trennschaukel and two-bulb methods; isotopic vapor pressures; mutual diffusion coefficients; total and differential atomic scattering cross sections; fundamental atomic interactions by evaluation of the intermolecular potential.

123. ISOTOPE SEPARATION RESEARCH \$250,000 02-2
AND DEVELOPMENT
B. E. Jepson, E. D. Michaels,
W. M. Rutherford

The purpose of this program is the investigation of isotope separation by liquid phase thermal diffusion and by chemical exchange. Factors being investigated include: influence of vertical temperature gradients and coolant hydrodynamics on the behavior of thermal diffusion columns; isotopic thermal diffusion factors of chlorine, bromine, and sulfur compounds; isotopic separations of dissolved salts; multiple column liquid thermal diffusion cascades; application of action exchange membrane electrolytic reactors to closed reflux of chemical exchange systems: isotope exchange kinetics at high pressures; separation of metal isotopes (calcium, lithium, and iron) by chemical exchange with polyethers.

124. SURVEY OF ISOTOPE \$ 65,000 02-2
APPLICATIONS
R. DeWitt, V. L. Avona

The objective of this project is to survey the current applications of enriched isotopes and project future requirements of these isotopes in the general fields of application; i.e., (1) nuclear, (2) environmental (3) biological and medical, (4) agricultural, (5) geological, and (6) industrial.

NOTRE DAME RADIATION LABORATORY (Continued)

126. CHEMICAL PHYSICS OF REACTING SYSTEMS \$118,000 01-1
J. J. Kozak, M. Schwartz

The methods of quantum mechanics, statistical mechanics and nonequilibrium thermodynamics are being used to interpret phenomena and chemical-dynamic processes of interest in radiation chemistry, both at the molecular and macroscopic levels, and the approaches that have been developed are being extended to provide information of general interest in areas of chemistry and chemical physics. In the area of quantum mechanics, new methods are being developed for performing electronic structure calculations. These include model potential methods, a self-consistent-field valence bond theory, and direct methods for examining ionization phenomena as well as studies on exchange interactions. In addition, standard existing methods are being used to study problems in the areas of molecular structure, chemisorption, cluster stability, high temperature vapors, electron-solvent interactions, electron binding energies, photoionization cross sections, spin densities in radicals, and various spectroscopic properties. The dynamical aspects of the interaction of radiation with matter, and in particular, the temporal decay of excited states of two- and three-level atomic and molecular systems, are being investigated in an a priori sense via an analytical study of the time-dependent Schrodinger equation. The methods of nonequilibrium thermodynamics and nonlinear kinetics are being applied to studies of cooperative effects associated with coupled chemical reactions in micellar systems.

NOTRE DAME RADIATION LABORATORY (Continued)

127. CHEMICAL STUDIES OF RADIATION \$241,000 01-1
INDUCED REACTIONS
R. H. Schuler

Chemical approaches are used to examine radiation induced reactions with emphasis being on establishing detailed mechanisms which include proper descriptions of the effects of track structure and ion and radical recombination processes on the overall chemistry. Currently liquid chromatographic methods are being used extensively to examine the products formed in the radiolysis of aqueous solutions. Emphasis is on aromatic systems where addition, abstraction and competitive scavenging reactions can be examined. Information from these studies is coupled with that from optical and conductometric pulse radiolysis and from ESR studies on the reaction intermediates to give as complete a description as is possible of the course of radiation chemical reactions in aqueous solutions. Advantage is taken of presently available computational methods to simulate the course of radiation chemical reactions so that the effects of finite conversion can be properly taken into account to establish accurate initial yields and reaction rates. It has been shown that information from studies of the effect of solute concentration on product formation (chemical scavenger studies) can be transformed to give descriptions of the time dependence of intermediates and this approach is used to examine track and ion recombination processes. These descriptions are directly applicable to irradiations carried out with heavy particles and are particularly important in any attempt to use heavy particle radiation.

NOTRE DAME RADIATION LABORATORY (Continued)

128. RADIATION CHEMICAL AND PHOTOCHEMICAL STUDIES OF REACTIONS AT CHEMICAL INTERFACES
J. K. Thomas

\$138,000

01-1

Studies of radiation chemical and photochemical effects in micellar systems which emphasize the unique catalytic or inhibitive effects of micellar isolation and also the transport of reaction intermediates across interfacial barriers are in progress. These studies are of basic interest to both radiation chemistry and radiation biology and offer promise of providing methods for controlling the deposition of energy in photochemical and solar energy applications. Catalytic properties of the micelles result, in many cases, from the considerable electrical potential at the interface (some 100,000 volts) which can enhance or decrease the rate of chemical reactions by a 1000 fold or more. Where reactants are charged, the effect of the micellar structures on the rate depends on the relative sign of the reactant and micellar charge so that one can control the reaction by proper choice of micellar material. In some instances electron transfer reactions which do not occur in homogeneous solution can be generated at the micelle interface. In other cases it has been possible using micelles to prevent reaction⁴ by keeping the charges on the reactants separated for times at least 10^4 times longer than is possible in homogeneous solution. Qualitative changes in the chemistry can be produced as a result of profound changes in the lifetime and/or ionization potential of the reaction intermediates. These studies are aimed at determining the way in which the reaction is controlled by the aqueous-lipid interface and at developing micellar methods to examine kinetic details of chemical reactions. Experimental methods used include standard pulse radiolysis and laser photolysis approaches as well as appropriate back up chemical experiments.

NOTRE DAME RADIATION LABORATORY (Continued)

133. ENERGY TRANSFER IN ATOMIC AND MOLECULAR SYSTEMS
D. H. Winicur

\$ 56,000

01-1

The goal of this research is to use molecular beam methods to determine the mechanisms, cross sections, and intermediate species involved in the transformation of energy from one form to another. Crossed beams are being used to measure differential scattering of electronically-excited metastable rare-gas atoms by various small molecules (e.g. H_2O , CO_2 , HBr , C_6H_6 , N_2 , Br_2). Time-of-flight techniques are employed to measure the velocities and the identities of the scattering species. These experiments provide detailed information on the cross sections for energy transfer between atoms and molecules, indicate the states formed immediately after the initial energy transfer, and allow a determination of the potential-energy curves for the interacting atoms and molecules. Some of the problems currently under study include examination of the magnitudes and velocity dependences of the integral electronic energy exchange cross sections between excited rare gas atoms and small molecules. These cross sections are determined by examining the quenching of the differential scattering at large angles. Potential-energy curves for the electronically-excited states of atom-molecule complexes are being determined in order to examine the qualitative differences between these and the ground-state curves. Detailed studies are in progress on the effects of the initial relative kinetic energy and of the electronic excitation energy of the atom on the transfer of energy to small molecules. Understanding of energy transfer mechanisms is of importance to the development of chemical lasers and we plan to extend these studies to a wide variety of energy transformations of interest to radiation, laser, and atmospheric chemistry. A strong effort is currently underway to investigate various aspects of translation-rotational energy transfer.

NOTRE DAME RADIATION LABORATORY (Continued)

134. PHOTOISOMERIZATION

\$111,000

01-1

A. M. Trozzolo

Photochemical studies are being carried out on a variety of organic systems in order to study the mechanism by which the absorbed light energy ultimately produces chemical effects. Understanding photochemical mechanisms is, of course, essential to any attempt to use photochemical methods to store solar energy as well as to understand the photostability of the materials which might be involved. Photochemistry allows one to inject energy into a system in a well-defined manner and to study the nature of intermediates and products by a variety of techniques. Current research is concerned with the valence isomerization of heterocyclic compounds, the chemistry of ground state-triplet molecules (produced photochemically), electron-transfer reactions of singlet oxygen and superoxide anion, and the excited-state reactions of laser dyes. The studies on heterocyclic compounds involve a number of photochromic systems in which a relatively strained ring is opened photochemically to produce a high energy intermediate, whose stability can be controlled. It is expected that these systems may serve as models for energy storage devices. The electron transfer reactions of singlet oxygen and superoxide anion are being studied in view of the important role that these species play in photooxidation, photobiology, chemiluminescence and enzymatic reactions. The excited-state reactions of coumarin dyes are being studied in an effort to understand the nature of the luminescent species responsible for the wide-tunability of dye lasers employing these compounds.

NOTRE DAME RADIATION LABORATORY (Continued)

135. RADIATION CHEMISTRY DATA CENTER \$ 64,000 01-1
A. B. Ross

The objectives of the Radiation Chemistry Data Center (RCDC) are the continuous survey of the literature of radiation and photochemistry, the assembly of appropriate bibliographic information on computer readable keyworded files and the critical examination and compilation of experimental data on radiation produced reaction intermediates. The computer-assisted systems developed for storage and retrieval of the pertinent literature references make possible a variety of information services including literature searching, preparation of current-awareness aids and bibliographies. Bibliographic publications issued regularly are the Biweekly List of Papers on Radiation Chemistry and its annual cumulations and indexes. This current-awareness service is of important use to other radiation chemical and related efforts supported by DOE. The data compilation activities are aimed at producing evaluated compilations of kinetic and spectroscopic information on reaction intermediates. Requests from individuals for particular types of data are answered. As the referenced areas mature, these compilations are made available to interested scientists by publication in the NSRDS-NBS series. Examples published to date are summaries of rate information on the reactions of hydrogen atoms (NSRDS-NBS No. 51), hydroxyl-radicals (NSRDS-NBS No. 59) and hydrated electrons (NSRDS-NBS No. 43). The critically reviewed data are of general importance to proper consideration and technological application of chemical processes involving reaction intermediates and it is of vital importance to chemistry to develop an expanded basic set of such information.

NOTRE DAME RADIATION LABORATORY (Continued)

136. ORGANIC PHOTOCHEMICAL PROCESSES \$101,000 01-1
 J. C. Scaiano

This research is directed toward understanding photochemical processes involving biradicals and the reactions of photolytically produced oxygen centered free radicals. Biradicals are common reaction intermediates, but their rate and reactivity is presently poorly understood. Our studies are aimed at the elucidation of the mechanism of the reactions of these intermediates. The problems under study include the photochemistry of aromatic ketones which yields biradicals of the type: $\text{PhC(OH)CH}_2\text{CH}_2\text{CR}_2$, which can be studied using laser flash photolysis techniques.² This type of biradical is responsible for many examples of polymer photodegradation and is also capable of undergoing a variety of electron transfer reactions. A noteworthy characteristic of these is the early (nanosecond time scale) intramolecular conversion of electronic into chemical energy, which leads to highly efficient electron transfer processes without the common requirement of a long lived excited state. This feature is of interest from the point of view of the conversion of radiant into chemical energy and is rather common in natural photoprocesses. A second part of our current research involves the study of the reaction kinetics of oxygen centered free radicals which are important intermediates in organic, biological and atmospheric chemistry. These studies are aimed at the determination of absolute rates of reaction. The initial studies center on alkoxy radicals produced in the photocleavage of organic peroxides, but it is planned to include other oxygen centered free radicals, e.g. acyl-oxy. Typical substrates include hydrogen donors and organometallic compounds.

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138. RD&D: ADVANCED CHEMICAL MEASUREMENTS TECHNOLOGY \$245,000 02-3
C. Feldman, J. E. Strain,
J. P. Young, R. W. Stelzner

The objective of this project is to utilize emerging technology from all scientific disciplines to extend the limits of chemical measurement methodology. Particular emphasis is given to techniques that result in increased speed, efficiency, accuracy, lowered detection limits, and multicomponent analysis. A previously designed arc emission detector is being combined with a new background correcting system for use in gas chromatography. This combined detection scheme is being used to eliminate spectral interferences from organic compounds in multicomponent analyses. The system is also being used to study organo-fluorine materials. Work on the basic chemistry, radiochemistry, and spectroscopy of the transuranium elements continues. A new effort is being initiated in the area of laser induced fluorescence and its application to the analysis of materials at the picogram level. First work is directed towards the development of supersonic beam fluorescence for gas phase analysis.

139. MASS SPECTROMETRIC R&D FOR INORGANIC AND ACTINIDES ANALYSES \$140,000 02-3
R. L. Walker, D. H. Smith,
D. L. Donohue

Major efforts and goals of this project are inorganic mass spectrometry using thermal emission mass spectrometry (TEMS) and spark source mass spectrometry (SSMS). These studies include: improved ion detection systems and ion sources for SSMS (computer-controlled vidicon read-out); investigation of rf spark parameters leading toward speciation and compound identifications for SSMS; further development in small-sample analysis using exchange-resin beads, applicable to energy, environment, and safeguards; improved surface ionization measurements by investigating parameters such as sources, source geometry, scanning modes, and detectors for TEMS; improvements in electronics and computerization for TEMS instruments which will provide more flexibility and improve precision.

OAK RIDGE NATIONAL LABORATORY
Analytical Chemistry Division (Continued)

140. ION MICROPROBE MASS ANALYZER \$110,000 02-3
R&D; SURFACE CHARACTERIZATION
W. H. Christie, R. E. Eby,
R. W. Stelzner

The ion microprobe mass analyzer (IMMA) provides a unique analytical capability in the areas of surface analysis, diffusion studies, depth profiling, and isotopic elemental analysis. The extreme sensitivity of secondary ion mass spectrometry (SIMS) makes it most 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 secondary ion mass spectrometric data, and demonstrate the applicability of SIMS to the solution of surface analytical problems in on-going DOE research programs.

141. MASS SPECTROMETER R&D \$135,000 02-3
FOR ORGANIC ANALYSIS
W. T. Rainey, D. C. Canada,
J. C. Franklin

The objectives of this project are: (1) to conduct organic mass spectrometry and separations research leading to superior methodology for identification and quantification of organic constituents in complex organic mixtures, (2) to study ionization processes in order to develop improved ion sources and associated components so that mass spectrometers can be more effectively used in organic analyses, and (3) to study techniques whereby specific organic functional groups and/or structural configurations can be uniquely identified by mass spectrometry.

OAK RIDGE NATIONAL LABORATORY
Analytical Chemistry Division (Continued)

142. ADVANCED SPECTROMETRIC METHODS \$220,000 02-3
FOR CHEMICAL ANALYSIS
L. D. Hulett, J. M. Dale,
R. W. Shaw, L. N. Klatt

The objective of this effort is state-of-the-art spectroscopic methods for general application. Four subtasks are currently under investigation. (1) Rapid scan spectrometry is being developed for simultaneous, multicomponent atomic and molecular analysis. This technology will increase the speed and efficiency of analysis for complex sample systems. Applications being studied include molecular absorption for liquid chromatography detection and atomic emission from microwave excited plasmas used with gas chromatography effluents. (2) A laser excited opto-acoustic spectrometer is being designed and fabricated for applications evaluation. This system will have the ability to provide unique spectral information for materials (opaque, metals, surfaces, etc.) that cannot be studied by conventional techniques. The completed opto-acoustic system will be used initially to analyze for materials in coal (in the solid state) and will also be used to study liquefaction materials that exhibit no fluorescence spectrum. (3) Electron spectroscopy (ESCA, Auger, electron diffraction) methods are being devised and two new electron spectrometers are being constructed. (4) Analytical applications of x-rays are being studied. These include the design, construction, and use of more sensitive x-ray diffraction apparatus for compound identification in environmental samples and other matrices. In x-ray fluorescence an absolute method for analyzing alloys by x-ray fluorescence is being extended to other types of samples.

OAK RIDGE NATIONAL LABORATORY

Chemical Technology Division

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143. CHEMISTRY OF SELECTED FISSION PRODUCT ELEMENTS \$120,000 02-1
J. C. Mailen

Provide basic data primarily applicable to the development of nuclear fuel recycle operations. Activities involve both devising new chemical processes and solution of problems which arise in existing processes. Current studies emphasize uranium and fission products transfer kinetics associated with Purex and Thorex solvent extraction systems.

144. KINETICS OF ENZYME-CATALYZED PROCESSES \$120,000 02-1
B. Zane Egan

Investigation of kinetics and enzyme catalysis related to hydrogen and ammonia production and energy production processes; catalytic processes for environmental control of waste effluents; hydrogen production from photo-oxidation; optimization of reaction rates; isolation, purification and stabilization of enzymes and substrates; kinetics of redox reactions of ferredoxin.

145. CHEMICAL ENGINEERING RESEARCH \$370,000 02-2
S. D. Clinton, R. M. Canon,
B. R. Rodgers, J. M. Begovich

Evaluation of mass transfer in three-phase fluidized beds, pertinent to design of coal conversion and biochemical reactors. Investigation of continuous chromatographic systems for recovery and purification of relatively large quantities of chemical components. Study of mechanisms by which very small particles can be agglomerated (for difficult solid-liquid separations). Investigation of slagging and other chemical processes for the recovery of materials from scrap.

OAK RIDGE NATIONAL LABORATORY
Chemical Technology Division (Continued)

146. TRITIUM SEPARATION TECHNOLOGY \$155,000 02-2
P. W. Fisher, S. D. Clinton

Tritium sorption on yttrium from liquid lithium in static systems; investigation of flowing system to reduce the liquid phase mass transfer resistance (impact on fusion reactor blanket processing systems). Measurement of equilibrium sorption isotherms for molecular sieves (5A, 13X, and NaY) at temperatures down to 4.2 K; cryosorption pumping rates for hydrogen isotopes and helium for fusion reactors. The objective of this program is to obtain fundamental information on separation of tritium from materials proposed for fusion or fission reactors.

147. SEPARATIONS SYSTEMS RESEARCH \$385,000 02-2
C. F. Coleman, W. J. McDowell

Origination and investigation of new, potentially useful separations agents and methods and improvements of existing methods; compilation and interpretation of the associated descriptive chemistry; application to specific process needs. Problem areas in nuclear fuel cycle (ores, spent fuel, wastes), coal technology, resource recovery. Separations of (principally) metal ions, also other inorganic, organic, biological values. Systematic studies of pertinent aqueous systems, such as extractions of weak acids (H_2CO_3 , H_2SO_3 , H_2S , phenols, carboxylic acids) and extraction of species from such weak acids.

148. WASTE STREAM PROCESSING \$230,000 02-2
STUDIES
M. H. Lloyd, J. B. Knauer

This project involves studies of reactor fuel reprocessing solutions and of subsequent high-level waste streams from fuel reprocessing plants. These studies include (1) an investigation of the nature of inextractable plutonium in fuel reprocessing and high level waste streams and methods of removal; (2) the identification of mechanisms and conditions that produce actinide losses in reprocessing solutions; (3) evaluations of interactions that can produce interfacial solids and emulsions during extraction and stripping operations; and (4) control of neptunium and plutonium valences using alternate reductants more amendable to reagent recycle concepts and waste-solidification processes. These studies give attention to identification and evaluation of process methods for isolating selected isotopes or fission-product elements which seriously complicate fuel-reprocessing and waste-handling operations, and to removing long-lived hazards from intermediate and low-level waste streams generated by the reprocessing of spent fuels and by other operations in the nuclear fuel cycle.

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150. RADIATION CHEMISTRY AND PHOTOCHEMISTRY \$175,000 01-1
C. J. Hochanadel, T. J. Sworski

This research is concerned with the study of chemical kinetics by direct observation of transient changes both on a microseconds time scale (conventional flash photolysis) and on a nanoseconds time scale (pulsed laser photolysis and pulse radiolysis). Most of the effort is on studies of gaseous systems with particular emphasis on those intermediates (small free radicals) that are important in combustion, coal gasification, and atmospheric chemistry. There is a small continuing effort on the study of aqueous solutions, with emphasis on those intermediates that are important in reactor technology, and/or the conversion and storage of solar energy.

151. SOLAR PHOTOCHEMICAL CONVERSION PROCESSES \$145,000 01-1
R. M. Pearlstein

The discovery of the three-dimensional arrangement of chlorophylls in purified chlorophyll-proteins that are associated with isolated photosynthetic reaction center complexes opens a new avenue to explore the photophysics and photochemistry of these molecular aggregates. Using various optical spectroscopies, as well as theoretical analyses, the relation of the optical properties to the structure of such aggregates are being investigated in order to understand the electronic excited-state behavior of stably photoactive chlorophyll. By learning which aspects of biologically-derived structure are critical to this behavior, it is hoped to design model (nonbiological) chlorophyll systems that mimic the stable photophysics and photochemistry of the natural systems. This approach differs from others that attempt to model only the photochemical behavior of photosynthetic reaction centers, whose structure is not precisely known. Non-laser spectroscopic techniques employed include ordinary absorption and fluorescence, electric-field-oriented and microcrystalline linear dichroism, cryogenic absorption, derivative absorption, and light-minus-dark difference absorption. Laser techniques include site-selection spectroscopy (absorption-fluorescence double resonance) and hole-burning spectroscopy. Theoretical analyses include exciton-theoretic computer calculations based on specific chlorophyll geometries and molecular orbital calculations to model the interaction of chlorophyll with axial magnesium ligands.

OAK RIDGE NATIONAL LABORATORY
Chemistry Division (Continued)

154. PHOTOCHEMICAL, PYROLYTIC, AND REACTIVE INTERMEDIATES BY ELECTRON SPIN RESONANCE
R. Livingston, H. Zeldes \$190,000 01-2

Chemical free radicals in fluids are being studied by electron spin resonance. Methods of forming radicals include photolysis, pyrolysis, and chemical reaction in molten salts. Many of the radicals made are highly reactive with lifetimes ranging down to less than a millisecond; in these cases the radicals are observed at steady state concentration being formed continuously as the fluid flows through the spectrometer. The spectra usually consist of very sharp, well resolved lines from which radicals may be identified and features of their electronic structure elucidated. Often a radical is studied with changes in the nature of the liquid (temperature, pH, solvent, etc.) and much is often learned about mechanisms of reactions, motional effects, exchange of protons, pK for ionization, etc. Kinetic studies on the rates of formation and disappearance of radicals are also being made. The purpose of this work is to use electron spin resonance to help develop the chemistry of free radicals which includes photolytic, pyrolytic and chemical processes through which they are formed and their identification and properties once they have been formed.

155. THEORETICAL CHEMISTRY
O. H. Crawford, D. W. Noid \$ 75,000 01-2

This program has two objectives: (1) to develop at ORNL a strong capability in theoretical chemistry and (2) to give theoretical guidance and support to the experimental programs. There is at ORNL a variety of experimental work investigating atomic and molecular structure, and chemical reactions, where theory and experiment will reinforce each other. This work is in areas such as molecular beams, electron and ion collision physics, photoelectron spectroscopy, x-ray and neutron diffraction, microwave spectroscopy, Raman spectroscopy, ESR and NMR spectroscopy, and photochemistry. All of these generate data which are valuable to quantum chemistry or statistical mechanics. Theory is used to calculate chemical reaction cross sections, energy distribution in reaction products, potential energy surfaces for atomic and molecular collisions, molecular spectra, and structures of molecules and ions.

OAK RIDGE NATIONAL LABORATORY
Chemistry Division (Continued)

156. ORGANIC CHEMISTRY AND THE CHEMISTRY OF FOSSIL FUELS \$440,000 02-1
B. M. Benjamin, V. F. Raaen,
R. M. Jones, E. W. Hagaman

Identification of "Scissile Bonds" cleaved during coal conversion at 400°, with hydrogen donors, to preasphaltenes, asphaltenes, oils; study of bond cleavage as a function of structure and donor reagent systems; find better means to attack bonds leading to coal liquefaction. Determine aromaticity. Use ¹⁴C-labeled reagents to investigate structural features and reactivity of separated vitrinite and whole coals; relate coal reactivity using compounds with structures analogous to those in coal. Establish the mechanisms of the free radical processes. Identify products by gas chromatography, radioactivity assay, proton and carbon-13 NMR spectroscopy. Establish solid state NMR project to study bonding in coal and coal products. Study of organic reaction mechanisms not necessarily related to coal or fossil fuels.

157. MOLTEN SALT CATALYSTS FOR CLEAN FUEL SYNTHESIS \$295,000 02-1
G. P. Smith, A. S. Dworkin,
J. Brynstad, L. O. Gilpatrick

Catalytic chemistry in molten salts. Hydrogenation, dehydrogenation, condensation, protonation and one-electron oxidation of polycyclic aromatic compounds in molten antimony trichlorides; effects of added Lewis and protonic acids and bases, and of oxidants and reductants; investigated by optical spectroscopy, electron spin resonance, nuclear magnetic resonance, and cyclic voltammetry of the melt, and byproduct separation from the melt. This project is a fundamental investigation 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. Attention is focused on specific model systems which are studied in depth using a variety of experimental methods. These include direct observations of the molten solutions by means of ESR, NMR, optical spectroscopy, and electrochemical methods as well as more or less conventional analytical techniques leading to the separation and identification of the reaction products.

OAK RIDGE NATIONAL LABORATORY
Chemistry Division (Continued)

158. RESEARCHES ON THERMAL GENERATION OF HYDROGEN
C. E. Bamberger \$150,000 02-1

Study of hydrogen cycles for the production of hydrogen from water by thermochemical reactions; includes research on new or improved chemical reactions, new chemical compounds, thermodynamic data, and process kinetics to develop economical thermochemical cycles, work and heat requirements, materials compatibility; possible uses of solar energy as heat source, synthetic fuels and energy storage. To further the development of efficient and economical cycles, research is directed at the basic inorganic chemistry involved in identifying new compounds and reactions, and in estimating their thermodynamic parameters. Additionally, kinetic data and compatibility of the reagents and products with container materials are sought. Although the emphasis is on reactions that can occur at temperatures achievable with a dedicated nuclear source, reactions that could occur at higher temperatures, e.g., those attainable by solar energy, are also examined.

159. AQUEOUS CHEMISTRY AND THERMODYNAMICS TO ELEVATED TEMPERATURES AND PRESSURES
H. F. Holmes, M. H. Lietzke,
W. L. Marshall \$360,000 02-1

Thermodynamics of aqueous systems at elevated temperatures and pressures for technological applications using potentiometry, conductance, isopiestic experiments, heat flow microcalorimetry, and solubility measurements; understanding of effects of temperature and pressure on equilibria, acid-base buffering systems, and electrolyte behavior; basis for accurate equations of state; hydrolysis and solubility of metal ions; solutions of alkali and alkaline earth halides; impact on steam generators, reactor coolants, geothermal chemistry, environmental chemistry, and processing chemistry. Major current thrusts of the project are on the solubilities of oxides to provide information on the speciation and thermodynamics of metal ions at high temperatures and the isopiestic and heat-flow calorimetric methods to advance the knowledge of thermodynamics of electrolytes at high temperatures. The latter is a new approach which is expected to be applicable at supercritical temperatures.

OAK RIDGE NATIONAL LABORATORY
Chemistry Division (Continued)

162. FUNDAMENTALS OF SEPARATIONS \$180,000 02-2
CHEMISTRY
 W. D. Arnold, F. J. Hurst

Chemical knowledge of important separations methods, their mechanisms and applications. Investigation and improvement of methods for the studies; preparations and purifications; application of fundamental information to separations process development. Continued improvement of process for uranium recovery from wet-process phosphoric acid. Thorium resource recovery. Difficult-pair separations (Zr-Hf; Ta-Nb) using high pressure liquid chromatography. The purpose of this project is to increase the chemical knowledge of important separations methods, to understand their mechanisms, and to improve, extend, or define the limits of their applications. It includes investigation and improvement of the methods used for such studies, preparation and purification of selected materials, and application of the information obtained from these fundamental studies to the development of viable separations processes.

163. SPECTROPHOTOMETRIC STUDIES OF \$160,000 02-2
SOLUTIONS WITH ALPHA-ACTIVE
MATERIALS
 L. M. Toth, J. T. Bell

Chemistry of actinides and fission products under conditions related to development of nuclear fuel cycles. Redox, photochemical, corrosion reactions; distribution coefficients. Demonstration of reversible (light-dark) photosensitive redox reaction in aqueous solution. Photochemistry of uranium and plutonium in selected aqueous solutions; application to separation method and to improvement of fuel reprocessing. Chemistry of gaseous fission products. Plutonium polymerization in nitric acid solutions. The major purpose of this project is to investigate the chemistry of the actinides and of nuclear fission products over a wide range of experimental conditions, and to produce information relative to the problems and development of nuclear fuel cycles.

OAK RIDGE NATIONAL LABORATORY
Physics Division

P. H. Stelson - Phone: (FTS) 850-6402 or (615) 483-8611 Ext. 36402

166. MOLECULAR RESEARCH WITH ELECTRON SPECTROSCOPY \$170,000 01-3
 T. A. Carlson, W. B. Dress

Develop the potential of electron spectroscopy for application to molecular physics and general chemical behavior; use of electron spectroscopy in the study of molecules on surfaces; through the combined use of x-ray, uv and photon induced Auger spectroscopy, to obtain unique information about the chemical bonding of molecules adsorbed onto cleaned surfaces, including the spacial orientation of molecules relative to the surface plane, and the molecular orbitals responsible for the bond; to make as rapid use as possible of new discoveries in the basic field of electron spectroscopy, a cooperative program with members of the heterogeneous catalysis group.

167. COLLISION OF LOW-ENERGY MULTICHARGED IONS \$ 90,000 01-3
 C. F. Barnett, D. H. Crandall

Using the unique ORNL multiply charged ion source, these studies are confined to making benchmark measurements of electron ionization and excitation cross sections, as well as charge-exchange cross sections for velocities less than 1×10^8 cm/sec. These benchmark measurements are folded into Maxwellian distributions to obtain reaction rates. Comparison of these rates with rates determined from theta pinches and theory provide confidence in calculating the many rates needed in laboratory plasmas, astrophysics, and x-ray laser development.

168. HEAVY ION ATOMIC RESEARCH \$230,000 01-3
 P. D. Miller, C. D. Moak

The objectives of this accelerator-based research are the detailed understanding of a broad class of phenomena occurring when multiply-charged heavy ions interact with gases, solids, and free electrons. Observations and measurements are made of: resonant coherent excitation of channeled ions; stopping powers of heavy ions in crystal channels, in gases, and in solids; excited state lifetimes of multiply-charged heavy ions; electron ejection from solids; ion stripping in gases and solids; electron capture by multiply-charged heavy ions incident on atomic and molecular hydrogen; coulomb excitation, molecular orbital promotion, and direct electron capture mechanisms for inner-shell excitation of heavy atoms; quasi-molecular x-ray studies; interactions of multiply-charged heavy ions with free electrons; and ionic and excitation states in crystal channels.

OAK RIDGE NATIONAL LABORATORY
Physics Division (Continued)

169. MOLECULAR INFRARED SPECTROSCOPY \$ 70,000 01-3
H. W. Morgan

In the infrared spectra region, this continuing research project on the solid state emphasizes the behavior of dopants and impurities in solids, the formation of solid solutions by foreign ions in alkali halide lattices, and the occurrence of solid phase chemical reactions. These studies require high resolution infrared spectra at temperatures down to 4°K. These spectra are an important source of information on the behavior of solids under a variety of conditions. In submillimeter spectroscopy, the rotational spectra of small molecules, together with the Stark effects and energy shifts due to centrifugal distortion, are being examined and recalculated in an effort to improve the power output of existing far infrared lasers and to extend the number of transitions on which laser action can be realized. The work involves the use of pulsed and continuous wave, submillimeter laser equipment now under development at ORNL.

170. THEORETICAL ATOMIC PHYSICS \$ 80,000 01-3
R. L. Becker

Calculations are performed and theories developed to account for important atomic processes, primarily those under experimental investigation at ORNL, with emphasis on cross sections and spectroscopy useful to the magnetic fusion energy and heavy-ion accelerator programs. At present, effort is concentrated on calculating charge exchange and ionization produced by energetic highly stripped ions colliding with atomic hydrogen, which are being measured at ORNL and are important as energy-loss mechanisms resulting from impurities in plasmas. Also the capability to compute spectra of multi-charged ions is being developed for use in the diagnostics and modeling of plasmas. Consulting and collaboration with experimentalists is an important activity expected to increase as theoretical tools are developed.

171. EN TANDEM OPERATIONS \$100,000 01-3
J. L. C. Ford, Jr.

Operation of EN-tandem Van de Graaff for atomic physics research; improvement of vacuum system; and, increase of the range of available ions.

PACIFIC NORTHWEST LABORATORY
P. O. Box 999
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Chemical Technology Department

R. E. Nightingale - Phone: (FTS) 444-7511 Ext. 946-2597 or (509) 946-2597
P. C. Walkup - Phone: (FTS) 444-7511 Ext. 946-2432 or (509) 946-2432
T. F. Demmitt - Phone: (FTS) 444-7511 Ext. 946-2330 or (509) 946-2330

172. STUDY OF REACTION MECHANISMS \$ 68,000 02-1
INVOLVED IN THE HYDROGENATION
OF COAL
J. A. Franz

The objectives of this work are: (1) to determine the mechanisms of hydrogen transfer to coal under conditions of thermal dissolution of coal in donor solvents; (2) to assess the role of free radicals in hydrogen transfer, condensation or fragmentation modes of organic molecules and skeletal rearrangement of organic molecules; and (3) to attempt to characterize the evolution of coal structure under conditions of thermal dissolution in donor solvents. Initial work has centered around photolytic generation of hydrogen-donor solvent-derived radicals and their characterization by esr techniques, thermal rearrangements of hydrogen donor radicals, and condensation of hydroaromatic radicals with aromatic systems. In order to understand the mechanisms of hydrogen transfer to coal, and the evolution of coal structure during dissolution, specifically deuterated hydroaromatic solvents are being used to reductively thermolyze coal in an attempt to characterize the molecular sites to which deuterium is transferred in the early stages of coal dissolution using ^2H FTNMR. Parallel kinetic studies of coal dissolution in tetralin and 1- ^{13}C -tetralin at 425°C using ^{13}C , ^{17}O and ^{14}N NMR and molecular weight distribution (gel permeation chromatography) are being carried out to monitor the evolution in structure as coal dissolution progresses. In order to probe the potential for radical-mediated rearrangements of organic radicals under coal dissolution conditions, the vacuum pyrolysis of hydroaromatic radical precursors is being carried out, in conjunction with ESR studies of the structures of radicals that undergo rearrangements.

PACIFIC NORTHWEST LABORATORY
Chemical Technology Department (Continued)

173. CONVERSION OF CELLULOSIC WASTES \$120,000 02-1
INTO LIQUID FUELS
P. M. Molten

The purpose of this project is to define the reaction chemistry of aqueous thermochemical processes for direct conversion of cellulosic materials into liquid fuels, and to determine the effects of the principal process variables on the reaction chemistry and the properties of the reaction products. Significant progress has been made in identifying and correlating the effects of major operating condition and environmental chemistry variables on the reaction chemistry of cellulose, and on the types and amounts of liquid fuel products that can be produced by exposing this material to temperatures between 235 and 350°C and initial pressures of between 0 and 1500 psig (final pressures of between 500 and 4500 psig). An experimental strategy based on statistical design principles was employed to select the parameters for conversion of pure cellulose into oil. Analysis of the experimental results and the derivation of analytical data on the available oil products is well under way.

174. A FUNDAMENTAL INVESTIGATION OF \$ 84,000 02-1
HOMOGENEOUS CATALYTIC SYSTEMS
FOR SYNTHESIS OF HYDROCARBONS
FROM SYNTHESIS GAS
J. L. Cox

The purpose of this project is to study homogeneous systems that effect the reaction of H₂ with CO to produce hydrocarbons and oxygenated hydrocarbons. The reaction of H₂ and CO with molecular metal complexes, primarily of the transition metals, are being examined under a variety of experimental conditions, such as the reaction of Group VIII transition metal carbonyls with H₂ and CO at high temperatures (>200 C) and high pressures (500-700 atm). Carbonylation-decarbonylation reactions are being studied as possible mechanistic routes to the reduction of CO with H₂, e.g., decarbonylation of formaldehyde to produce CO and H₂ has been observed which affords an example of the reverse oxygenated hydrocarbon synthesis reaction. The chemical reduction of transition metal carbonyls with metal hydride complexes to form transition metal formyl complexes is being examined as well as the lability of transition metal carbonyls. Finally deoxygenation of CO in the presence of polynuclear complexes is being examined as yet another plausible pathway to hydrocabons from H₂ and CO.

PACIFIC NORTHWEST LABORATORY
Chemical Technology Department (Continued)

<u>175.</u> DEVELOPMENT OF PREDICTIVE MODELS FOR FLUIDIZED BEDS AND ENTRAINED SUSPENSIONS IN COAL CONVERSION C. T. Li, L. K. Mudge	\$ 75,000	02-4
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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 able to predict the performance of fluidized beds and entrained suspension reactors as functions of system size and configuration, chemical reactions and physical changes occurring within various coal conversion reactor systems are being developed.

PACIFIC NORTHWEST LABORATORY
Physical Sciences Department (Continued)

179. ULTRASENSITIVE MASS SPECTROMETRIC \$170,000 02-3
ANALYTICAL TECHNIQUES
C. R. Lagergren, R. L. Gordon

Improved utility of surface ionization mass spectrometry by increasing sensitivity and extending areas of analysis; fundamental understanding of surface ionization (sample impurities, filament interactions); development of direct-inlet mass spectrometry (ultrahigh sensitivity, real-time measurements); design, construction, and assembly of a simultaneous mass detection spectrograph.

180. HEAVY ELEMENT SEPARATION \$ 75,000 02-3
AND ANALYSIS TECHNIQUES
D. M. Robertson, J. M. Kelley

Development of analytical techniques with improved measurement sensitivity, selectivity, and accuracy for elements generated in nuclear power production; elucidation of limiting chemical factors in thermal ionization mass spectrometry; development of low background ion-source filaments; characterization of sample and filament interactions; use of analytical techniques in environmental impact, hazards assessment, process releases, national security, and waste management programs.

181. ULTRASENSITIVE RADIOACTIVITY \$ 85,000 02-3
SPECTROMETRIC ANALYTICAL
TECHNIQUES
F. P. Brauer

Development of ultrasensitive and selective radioactivity spectrometric techniques; exploitation of unique and extremely specific correlations between decay emissions; multiparameter nuclear spectrometric measurements of x-rays, gamma-rays, alpha particles, electrons, neutrons, and time relationships between decay events; improved data analysis, background reduction, and detector efficiency and selectivity; methods for in situ real-time determinations.

PACIFIC NORTHWEST LABORATORY
Physical Sciences Department (Continued)

182. ULTRASENSITIVE LASER-BASED \$ 85,000 02-3
SPECTROMETRIC ANALYTICAL
TECHNIQUES
R. W. Goles

Development of ultrasensitive and selective laser-based analytical techniques for detection, identification, and measurement of trace substances; detection and identification of chemical forms; laser operating and measuring modes: fluorescence, absorption, cavity-amplified absorption, cavity-induced selective extinction; frequency modulation techniques; digital and phase sensitive techniques along with photon source regulation and source compensation methods for sensitivity enhancement; frequency stabilization for selectivity enhancement; and photon correlation analysis.

SANDIA LABORATORIES/ALBUQUERQUE
P. O. Box 5800
Albuquerque, New Mexico 87115

Department 4210

J. B. Gerardo - Phone: (FTS) 475-3871 or (505) 264-3871

184. MHD ATOMIC PROCESSES \$ 70,000 01-3
D. P. Aeschliman, R. A. Hill

Studies of the spectral location of the potassium lines with particular emphasis on their detectability and isolation from spectral interferences in simulated coal-fired MHD channel flows. The spectral region under study ranges from the near ultra-violet to the near infrared wavelengths.

SANDIA LABORATORIES/LIVERMORE
Livermore, California 94550

Combustion Sciences Department

D. L. Hartley - Phone: (FTS) 532-2747 or (415) 422-2747

<u>185.</u> COMBUSTION DIAGNOSTICS RESEARCH P. Mattern, E. Jones	\$210,000	01-2
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The primary objective of the Sandia Combustion Diagnostics Research Program is to develop and evaluate innovative, nonperturbing methods for the detailed analysis of reacting gases. Ultimately, these techniques are to provide spacially and temporally resolved temperature, density, and velocity information on major and minor species in practical combustion systems, including flames, combustion chambers, and engines. It is intended that the components of this program will form the basis for in-house diagnostic research in the Combustion Research Facility.

<u>186.</u> COMBUSTION RESEARCH FACILITY- DEVELOPMENT AND OPERATIONS J. E. Marion	\$ 70,000	01-2
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The proposed activities in FY 79-80 are directed towards the assimilation of technical input to the design and construction of the Combustion Research Facility (CRF) and to specifying and developing the necessary equipment and staff for the Facility to begin operation in late FY 80. Efforts beginning in FY 78 and continuing throughout the period will include: (1) Diagnostic Development - This is the development, specification and acquisition of applicable diagnostic equipment for the CRF. (2) Facility Planning. (3) Facility Management and Operation - Before facility operation begins, management, operation, and safety procedures must be established. Special equipment must be installed and checked out.

SANDIA LABORATORIES/LIVERMORE
Combustion Sciences Department (Continued) .

187. COMBUSTION ANALYSIS BY \$220,000 01-2
ADVANCED RESEARCH METHODS
D. Hardesty, B. Sanders

This program will form the basis for the in-house combustion research studies in the Combustion Research Facility. The original objective of this program was the development and application of laser-based measurement techniques for experimental investigations of combustion processes. A complementary effort in sophisticated numerical modeling of reacting flow fields was incorporated as a program objective in FY 77. During FY 78 the program was extended to incorporate detailed experimental and mathematical studies of several fundamental combustion problems. Emphasis was placed on a limited number of research projects which permitted effective application of the continuing development of laser-based diagnostic techniques and computational methods. During this same period the diagnostic development activities have included the assessment, selection, and specification of special equipment to be housed in the Combustion Research Facility.

SECTION B

Other Government Agencies
Private Sector Corporations
Academic Institutions

The information in this Section was taken from current summaries and abstracts provided by the principal investigators. There is considerable (about 10%) turnover in these research projects and some will not be continued beyond the current contract period.

NATIONAL BUREAU OF STANDARDS/BOULDER

201. ATOMIC AND MOLECULAR COLLISION PROCESSES \$ 75,000 01-3
D. Norcross - Joint Institute
for Laboratory Astrophysics

Systematic studies of electron excitation mechanisms and scattering processes affecting energy conversion technologies are performed. Initial efforts focused on electron excitation and scattering by highly ionized atomic species in magnetic fusion plasmas; continuing efforts include calculations of electron scattering by polar molecules - a principal mechanism thought to significantly degrade coal-fired magnetohydrodynamic (mhd) conversion efficiencies. In the course of these studies sophisticated calculation techniques are developed. Special attempts are made to provide electron-ion cross-section data to scientists working with fusion and low temperature plasmas.

NATIONAL BUREAU OF STANDARDS/WASHINGTON

202. KINETICS DATA BASE FOR COMBUSTION MODELING \$ 65,200 01-2
W. Tsang, R. Hampson -
Physical Chemistry Division

The long range goal of this project is to develop a chemical kinetic data base of gas phase reactions for use in the modeling, design and optimization of energy conversion systems based on hydrocarbon combustion. In view of the diverse and complex nature of hydrocarbon fuels, the scope of this work ultimately encompasses all high temperature gas reactions involving C, H, O, N and S compounds of pertinence in a combustion context.

203. DETERMINATION OF SELECTED ATOMIC DATA PERTINENT TO THE CTR PROGRAM \$110,000 01-3
W. L. Wiese - Atomic and
Plasma Radiation Division

Calculations of both wavelengths and line strengths for heavy atoms for a large number of $n=0$ transitions, and resonance lines are made. These calculations include treatment of complex behavior along the sequence arising from the combined effects of configuration interaction and relativistic corrections. The \bar{g} -approximation used to calculate electron impact excitation cross sections (based on atomic oscillator strengths) is being assessed in detail. Dielectronic recombination studies are made and are focused on the detailed calculation of satellite spectra in beryllium-like oxygen. The ultimate objective is to develop a more refined, but still simple, formulation of this model of collisional excitation. Compilation and evaluation of highly ionized spectra of iron-group elements is executed and the systematic trend of such data along the isoelectronic sequences of Be, B, C, N, and O is being analyzed.

NATIONAL BUREAU OF STANDARDS/WASHINGTON (Continued)

204. STUDY OF CATALYTIC METHANATION \$140,763 02-1
REACTION OVER WELL-CHARACTERIZED
NI CATALYSTS AND LASER EXCITATION
OF ACTIVATED CHEMISORPTION
J. T. Yates, T. E. Madey, R. D. Kelley -
Physical Chemistry Division

Studies of the chemical reaction of carbon monoxide and hydrogen in the presence of high surface area metal catalysts, particularly nickel and ruthenium, through the use of modern surface measurement and kinetics techniques. High pressure kinetics; x-ray photoelectron spectroscopy (ESCA); Auger spectroscopy; mechanistic studies. Studies of laser excitation of activated chemisorption.

AEROCHEM RESEARCH LABORATORIES, INC.

301. HIGH TEMPERATURE PHOTOLYSIS \$ 78,000 01-2
 STUDIES OF COMBUSTION REACTIONS
 A. Fontijn - Reaction Kinetics Group

The goal of this program is to measure the rate coefficients of combustion reactions over a wide temperature range, i.e., from about 1800 to 300 K (2800 to 100°F) or to as low a temperature as is of practical interest. Prior to this work no technique capable of performing such measurements existed; indeed, for many pertinent reactions no techniques at all were available for making measurements at realistic temperatures. In order to fill this gap we are developing a new experimental technique, High-Temperature Photolysis (HTP). HTP combines two individually well-tested techniques: (1) the High-Temperature Fast-Flow Reactor we developed to study the kinetics of metal atom/oxide reactions over about the 300 to 1800 K temperature range and (2) the pulsed photolysis resonance fluorescence/absorption technique used in many laboratories for kinetic measurements of combustion intermediates (free radicals), but only near room temperature. The first HTP study concerns the reaction of oxygen atoms with methane, a reaction of major interest and one that is also conducive to development of the HTP technique. Subsequent studies will focus on reactions of increasing complexity, culminating in radical-radical reactions of higher hydrocarbon and oxidizer radical combinations.

AEROSPACE CORPORATION

302. TWO PHOTON PHOTODISSOCIATION \$ 77,000 02-2
 OF POLYATOMICS FOR ISOTOPE
 ENRICHMENT
 P. F. Zittel - Chemical Physics Department

Investigation of two-photon isotope separation techniques using infrared lasers to vibrationally excite molecules and ultraviolet lasers to photodissociate the excited isotopes; collection of photodissociation fragments by chemical reactions; theoretical model and experimental system for laser isotope separation of molecules containing ^{79}Br and ^{81}Br ; mass spectrometric sampling system for monitoring products.

AEROSPACE CORPORATION (Continued)

303. LASER-EXCITED NONRESONANT FLUORESCENCE SPECTROSCOPY \$ 37,990 02-3
J. A. Gelbwachs - Analytical Sciences Department

The objective of this project is improved elemental analysis by reduction of spectral interference effects from sample matrix components. In particular, experimental studies are being conducted to optimize SONRES (Saturated Optical Non-Resonant Emission Spectroscopy) detection of elements of analytical interest in the presence of more abundant elements commonly found with the trace analyte. As an example of interference for conventional resonance-fluorescence atomic analysis, spectral interference has been observed from a group of cobalt lines between 330 and 353 nm with the nickel line at 352 nm and interference to the platinum transition at 271.904 nm has been recorded by an iron line at 271.902 nm. The SONRES scheme appears particularly immune to spectral interference owing to the high specificity gained from narrow bandwidth optical laser excitation combined with narrow bandwidth optical nonresonance detection. SONRES also offers tremendous potential for the rejection of interfering signals from molecular components. Molecular cross sections are typically six orders of magnitude smaller than those of atoms and molecular fluorescence tends to be distributed over a much wider spectral width than atomic fluorescence.

BEND RESEARCH, INC.

304. COUPLED TRANSPORT MEMBRANES \$ 45,100 02-2
FOR URANIUM SEPARATIONS
H. K. Lonsdale - President

The effect of the nature of the exchanger, the effect of diluents, the make up of the rate limiting effect, the nature of the coupled ion, and the effect of external conditions such as pH, ionic strength and desired and contaminating ion concentrations on the flux and selectivity of liquid membranes, which are made by filling the pores of a microporous solid with a water immisible organic liquid complexing agent. A basic parametric study including both cation and anion transport.

GENERAL ELECTRIC COMPANY

305. INFLUENCE OF PHASE BOUNDARIES \$ 49,938 01-1
ON PHOTOINDUCED ELECTRON
TRANSFER REACTIONS
G. L. Gaines, Jr. - Corporate
Research and Development,
Schenectady, N.Y.

Experimental studies of photoinduced electron transfer reactions of ruthenium complexes and related compounds in the presence of phase boundaries, for the purpose of achieving useful charge separation. Preparation and characterization of Ru(bpy) complexes in both water soluble and surfactant forms, bearing overall positive, negative, and zero net charge; measurements of the luminescence quenching of Ru complexes as water soluble and surfactant derivatives in water, organic solvents, and in micellar aqueous solutions.

306. STUDY OF PHOTOCHEMICAL EFFECTS \$ 55,523 01-1
USING STABLE SEMICONDUCTOR
ELECTRODES
R. H. Wilson - Corporate Research
and Development, Schenectady, N.Y.

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 and the usefulness of the technique will be established.

ROCKWELL INTERNATIONAL/ATOMICS INTERNATIONAL DIVISION

307. MOLTEN SALT INTERACTIONS \$130,000 02-1
IN COAL PROCESSING
S. J. Yosim

Investigation of reactions in molten sodium carbonate; catalytic effects of sulfide and sulfate compounds in sodium carbonate on the air or CO₂ oxidation of different forms of carbon and of carbon in coal; reactions between typical coal ash components (alumina, iron oxides, iron sulfide, silicon dioxide, calcium oxide) and molten sodium carbonate; reactions of sodium and sodium-aluminum silicates with molten sodium carbonate; air oxidation of volatile hydrocarbons in molten sodium carbonate.

SRI INTERNATIONAL

308. ENERGY TRANSFER STUDIES \$ 60,000 01-2
 USING LARGE HIGHLY
 VIBRATIONALLY EXCITED
 MOLECULES
 J. R. Barker - Chemistry Laboratory,
 Physical Sciences Division

Experiments are underway for studying energy transfer processes from relatively large polyatomic molecules possessing high vibrational excitation in their ground electronic states. This is being accomplished by laser photoexcitation of azulene and/or some of its derivatives to the first excited singlet state, followed by extremely rapid internal conversion to produce vibrationally excited molecules in the electronic ground state. Once the excited molecules are prepared, V-T, V-V, and V-E energy transfer processes are studied by (1) time-dependent thermal lensing techniques (V-T), (2) I.R. fluorescence (V-V), and (3) visible fluorescence (V-E).

309. ATOMIC COLLISION PROCESSES \$ 30,000 01-3
 OF IMPORTANCE IN HEAVY
 ION INERTIAL FUSION PROGRAM
 R. E. Olson - Molecular Physics Center,
 Physical Sciences Division

This project is an investigation of $Cs^+ + Cs^+$ collision processes designed to determine the charge exchange cross sections. Self-consistent field (SCF) potential curves have been calculated for the relevant Cs_2^{++} molecular systems which indicate that the promotion of the $5p\sigma_u$ orbital to the highly excited $7f$ united atom limit determines the charge changing cross sections. Preliminary studies indicate that the charge changing cross section for $Cs^+ + Cs^+$ collisions is due to a simple one electron ionization process. The cross section associated with this process is estimated to be $4 \times 10^{-16} \text{ cm}^2$ at 100 keV and indicates that the Cs^+ system is not compatible with the use of a synchrotron for the acceleration system. Studies are being extended to multiply charged ion systems in the search for a more optimum projectile ion.

310. HIGH TEMPERATURE CHEMISTRY \$ 35,000 02-1
 OF HYDROGEN PRODUCTION CYCLES
 D. L. Hildenbrand - Physical
 Sciences Division

This research program consists of a study of the high temperature chemistry of a class of reactions which are common to a number of the more attractive thermochemical cycles for generating hydrogen; namely, the decomposition of metal sulfates. This includes both kinetic and thermodynamic property experimental measurements. Of particular interest is the observation that small amounts of Fe_2O_3 and other metal oxides affect significantly the decomposition pressure of $MgSO_4$. This research is expected to provide understanding of this catalyzed reaction which is relevant to the development of a viable sulfate cycle as well as pertinent thermodynamic values for the sulfates involved. In addition, the sublimation/vaporization and decomposition of K_2SO_4 is being studied because of the special importance to MHD and coal utilization technologies.

UNIVERSITY OF ALABAMA

401. ELDOR INVESTIGATIONS OF RADIATION PROCESSES \$ 43,386 01-1
L. D. Kispert, T. C. S. Chen,
Y. Hori - Chemistry Department

The objective of the present research is to examine the role of the host matrix as a function of temperature in determining the type and yield of radicals produced by X-irradiation of a crystalline or glass material using electron-electron double resonance (ELDOR), electron-nuclear double resonance (ENDOR), electron spin resonance (ESR) and heavy atom substitution techniques. Research on the effects of radiation on crystalline materials, along with the knowledge of the thermal history, nature of radiation, and the crystal structure or the form of the parent molecule is designed to predict what radical species will be stable at any given temperature. An examination of the ELDOR spectra of an irradiated substance results in a partial or complete measure of the relaxation mechanisms which, in turn, are related to the host matrix itself. The host matrix is changed by using the heavy atom substitution technique, by using different methods of crystallization, and by including radical precursors in clathrates and permits a study of the relation among host matrix variation, radical yield and relaxation parameters.

AMHERST COLLEGE

402. SOLVENT AND SOLUTE EFFECTS OF NON-REACTIVE GASES \$ 34,986 02-3
B. B. Benson - Department
of Physics

The precise determination of Henry coefficients of dissolved gases. Precise solubility data for He, Ne, Ar, Kr and Xe obtained previously in H₂O will be compared with similar data being obtained in D₂O. This will give us the opportunity to explore molecular interactions between isotopically substituted solute molecules with isotopically substituted solvents.

UNIVERSITY OF ARIZONA

403. MECHANISMS OF PHOTOCHEMICAL ENERGY CONVERSION BY CHLOROPHYLL \$ 45,000 01-1
G. Tollin - Department
of Chemistry

Photoinduced one-electron transfer reactions between chlorophyll and various oxidants are studied in solutions, polymer films and lipid bilayer membranes. Electron spin resonance and laser photolysis techniques are used to obtain insights into the mechanisms of these photoreactions, and to determine the factors which influence quantum yields and stabilization of the high energy photoproducts.

BOSTON UNIVERSITY (Continued)

407. ORGANIC PHOTOCHEMICAL STORAGE \$ 57,235 01-1
OF SOLAR ENERGY
 Guilford Jones, II -
 Department of Chemistry

The prospects for driving endoergic reactions of simple, relatively abundant organic chemicals by photochemical means have been examined. Strategies for utilization of light of varying wavelength involve sensitization mechanisms which depend on the redox properties of energy storing substrates and photosensitizers. Of principal interest is valence isomerization which can be induced by electron donor-acceptor interaction between substrate and sensitizer in an excited complex or exciplex. Completed photophysical studies show that potentially isomerizable substrates efficiently intercept redox photosensitizers. The quenching of emission of electron acceptor sensitizers by non conjugated hydrocarbon dienes is indeed a function of the reduction potential of the acceptors (a series of aromatics with varying absorption characteristics) and the oxidation potentials of the substrates. Electron deficient dienes have been shown alternatively to be efficient quenchers of excited donor sensitizers. That exciplexes are formed between isomerizable substrates and donor or acceptor sensitizers has been confirmed by emission spectroscopy. The rearrangement of hexamethyldeazarbenzene to hexamethylbenzene, a model exciplex isomerization has been examined in some detail. Photosensitization involving triplet energy transfer to isomerizable substrates has been examined. Using this technique the isomerization of a norbornadiene derivative having a large energy storage capacity has been successfully sensitized to visible light (wavelengths to 520 nm effective). The improvement of quantum efficiencies of photosensitized reactions involving highly endoergic triplet energy transfer at high temperatures has been initially assessed.

408. ELECTRON TRANSFER REACTIONS \$ 70,000 01-1
OF EXCITED DYES WITH METAL
COMPLEXES
 N. N. Lichtin, M. Z. Hoffman -
 Department of Chemistry

General objectives are to systematically study, correlate and interpret factors which determine quantum efficiency of transfer of reducing equivalents between excited dye molecules and metal complexes in their ground state as well as other factors which determine the composition and dynamics of formation and decay of the photostationary state of such photoredox systems. Aspects of interest include structures of dyes and ground state reagents, photophysical properties of dyes, ground state redox potentials of dyes and metal complexes, and the influence of solvent and solution composition on dynamic and steady-state properties. Assembly of apparatus for laser flash photolysis with 10^{-7} sec resolution is well advanced. A flash photolytic study of the kinetics of reaction of leucothionine and semithionine with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ has been completed. Evidence has been obtained for intermediacy of a leucothionine- $\text{Fe}(\text{III})$ complex. A number of features of the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ -methylene blue photoredox system have been investigated. Work on photoredox systems incorporating a stable complex of $\text{Fe}(\text{II})$ and thionine or methylene blue has begun.

BRANDEIS UNIVERSITY

409. HYDROGEN TRANSFER AND CHARGE \$ 35,000 01-1
TRANSFER IN PHOTOCHEMICAL
REACTIONS
S. G. Cohen - Department
of Chemistry

Studies of charge-transfer and hydrogen-transfer initiated by absorption of ultraviolet and visible light are being extended. Contributions of light absorption, quenching, and hydrogen-transfer by mercaptans and disulfides to retardation of photoreduction of ketones by alcohols are evaluated. Abstraction of hydrogen by aromatic and aliphatic ketyl radicals from mercaptans, and by thiyl radicals from alcohols are studied. Catalysis by aliphatic mercaptans of proton transfer in charge-transfer complexes (CTC's) of varied composition are studied. Mercaptan catalysis of photoreduction by thioethers and polyheteroatom donors, and effects of solvent on partitioning of CTC's between formation of radicals and return to ground state are studied.

410. PHOTOCHEMICAL REACTIONS OF \$ 92,782 01-1
COMPLEX MOLECULES IN
CONDENSED PHASE
H. Linschitz - Department
of Chemistry

This project is concerned with the mechanisms of photoredox processes and the factors leading to radical production versus energy dissipation. Using laser flash photolysis, dissipative quenching or recombination processes in liquids can be studied as a function of various parameters. Of particular interest are temperature, solvent polarity and viscosity, excited state multiplicity (singlet or triplet) and externally applied fields. In the case where triplet radical-pair recombination (requiring spin flip) competes with cage escape, magnetic fields increase the yield. The photochemical properties of chlorophyll dimers and aggregates are being studied, as possible models of the photosynthetically active forms of chlorophyll. A new "photodisaggregation" reaction of chlorophyll dimers, resulting from the weakening of coordinate bonds to the central magnesium ions in the excited state has been found.

BRIGHAM YOUNG UNIVERSITY

411. SEPARATION OF SELECTED CATIONS \$ 49,000 02-2
BY LIQUID MEMBRANES
J. J. Christensen -
The Thermochemical Institute

The study of the interaction of macrocycles with lanthanide cations in water-methanol solvents to establish the basis for lanthanide selectivity sequences. Particular attention is being given to the separation of trivalent lanthanides, Cs^+ and Sr^{2+} .

BROWN UNIVERSITY

412. INTERACTIONS OF MOLECULES WITH SURFACES \$ 55,000 01-2
E. F. Greene - Department
of Chemistry

The angular distribution of atoms scattered from a surface is sensitive to its structure. A beam of rare gas atoms is being velocity selected, scattered from a crystalline surface and velocity analyzed. The variation of the elastically scattered intensity with angle and kinetic energy E is being compared with calculations based on a simple model to relate features of the scattering to the structure of the surface. The formation of positive and negative ions when molecules strike surfaces of metals, semiconductors, and insulators is being studied to provide tests for the quasiequilibrium model for the process and to explore the effect of using resonance radiation to excite the incoming molecules. Preliminary work shows that the radiation can increase the yield of ions from Na on Al_2O_3 and that the equilibrium model is unsatisfactory. Study of this process and its dependence on E should reveal some of the dynamics as well as the energetics of the interaction and properties of the surface.

UNIVERSITY OF CALIFORNIA/BERKELEY

413. SURFACE CHEMISTRY AND CATALYTIC CHEMISTRY OF METALLIC SURFACES \$ 80,791 02-1
E. L. Muetterties - Department
of Chemistry

The structural and electronic characteristics of cyanogen chemisorbed on nickel and platinum surfaces are being established and the catalytic chemistry of these surfaces is being investigated. Single crystal faces, low and high Miller index faces, of nickel and platinum are being utilized as well as defined reference points. Metallic films treated with cyanogen are also being broadly examined for unique catalytic properties. This research uses an ultra high vacuum chamber and the requisite peripheral equipment.

UNIVERSITY OF CALIFORNIA/DAVIS

414. NUCLEAR METHODS IN
CHEMICAL KINETICS

\$ 60,000

01-1

J. W. Root - Department
of Chemistry

The research program includes classical kinetics studies of thermal ^{18}F elementary hydrogen abstraction and olefinic addition reactions; an experimental investigation of the effect of Ar moderator upon energetic F-for-F substitution reactions in CF_4 ; steady state hot atom kinetic theory model calculations; and the development of new analytical radiochemistry techniques. Thermal F-to-HF absolute rate constants are being determined for fast alkane hydrogen atom donors in order to provide a basis for the estimation of accurate molecular elastic collision cross sections. Competitive intramolecular absolute rate constants are being determined for F-to-HF vs. olefinic addition reaction channels in unsaturated hydrocarbons. Few such data are presently available. Existing unimolecular kinetics methodology is utilized in an investigation of the effect of Ar moderator upon the reactive collision energy distribution in the nonthermal ^{18}F vs. CF_4 system. Steady state kinetic theory model calculations are being carried out for the nonthermal ^{18}F vs. Inert Gas/ $\text{H}_2(\text{D}_2)$, $\text{H}_2(\text{D}_2)/\text{C}_3\text{F}_6$, $\text{CH}_3\text{CH}_3/\text{C}_3\text{F}_6$, $\text{CH}_3\text{CF}_3/\text{H}_2\text{S}$ and ^3H vs. $\text{O}_2/\text{D}_2/\text{CH}_4$ and $\text{O}_2/\text{H}_2\text{CD}_4$ systems.

UNIVERSITY OF CALIFORNIA/IRVINE

415. RESEARCH IN CHEMICAL
KINETICS

\$130,000

01-1

F. S. Rowland - Department
of Chemistry

This is a program which applies some of the methods developed for the study of hot atom chemistry to problems of interest to atmospheric chemists. Theoretical calculations, laboratory measurements, and field observations are performed which elucidate the behavior of halocarbons, hydrocarbons, and organometallic species in the atmosphere. Some specific topics being examined are as follows: (1) Absolute calibrations of electron capture detectors are being carried out for CCl_3F and CH_3CCl_3 , to permit accurate comparisons of atmospheric burdens with cumulative atmospheric release. (2) Ultraviolet absorption cross sections are being measured for CBrF_3 , $\text{CBrF}_2\text{CBrF}_2$, CCl_2O , CClFO and CF_2O , and their stratospheric significance assessed. (3) Thermal ^{38}Cl reactions are being studied with C_2H_2 and CH_4 at various pressures and temperatures, permitting assessment of stratospheric importance of these reactions. (4) Thermal ^{38}Cl reactions are being carried out with $\text{CH}_3\text{C}\equiv\text{CH}$ and other acetylenic substrates. (5) Thermal ^{18}F reactions are being studied with the isomeric butenes, and with organotin and organolead compounds. (6) Recoil tritium reactions are being studied with powdered graphite, and with SiC, Si and Ge.

UNIVERSITY OF CALIFORNIA/IRVINE (Continued)

416. INTERMOLECULAR ELECTRONIC ENERGY TRANSFER PROCESSES \$ 60,000 01-2
E. K. C. Lee - Department
of Chemistry

Rates and mechanisms of energy transfer and storage involving molecular excited states which are important in energy conversion processes. Excitation of molecular vibrations and rotations accompanying an intermolecular electronic energy transfer process are investigated to determine the resulting energy distribution and hence establish the physical and chemical mechanisms. The involvements of chemical quenching, charge transfer complex, excimer/exciple formation, isotope effect, reactive intermediates, long and short range interactions, etc., will be studied by luminescence spectroscopy and chemical kinetics.

417. STUDIES OF ISOTOPIC MASS EFFECTS IN CHEMISTRY \$ 59,700 02-2
M. Wolfsberg - Department
of Chemistry

Investigation of isotopic mass effects via isotopic effects on corrections to Born-Oppenheimer approximation; complete wave equation of molecular system. Experimental vs theoretical isotope effects on equilibrium constants. Energy transfer in collisions. Statistical mechanical perturbation theory to elucidate factors influencing isotope effects on chemical equilibria and chemical kinetics.

UNIVERSITY OF CALIFORNIA/LOS ANGELES

418. TIME RESOLVED RAMAN AND ENERGY TRANSFER STUDIES \$ 66,000 01-2
M. A. El-Sayed - Department
of Chemistry

Two new techniques are being developed to study the nature of the conformational changes occurring during the photosynthetic cycle of bacteriorhodopsin. A time resolved resonance Raman method is being developed to determine the vibrational spectra of both the chromophore and the protein in the different intermediates formed during the photosynthetic cycle. This is accomplished by using two pulsed tunable lasers, one for initiating the photosynthesis and the other for determining the Raman spectra. The changes in the molecular structure of the chromophore and the protein are determined from these studies. The changes in the intermolecular distances between the chromophore and protein sites during the cycle are studied by time resolved energy transfer processes between dyes bound to protein sites and the chromophore. By measuring the dye lifetimes at different delay times after the photosynthetic laser is triggered, the chromophore quenching efficiency for the dye excitation energy is determined for different intermediates. These time resolved studies will be extended to other photochemical and photobiological systems.

UNIVERSITY OF CALIFORNIA/LOS ANGELES (Continued)

419. CHEMISTRY OF HYDROCARBON SOLIDS AT HIGH PRESSURES \$ 52,000 01-2
M. F. Nicol - Department of Chemistry

Effect of pressure on chemical properties, reactions, optical spectra, and photochemistry of hydrocarbons; solids and fluid solutions; the absorption spectrum of anthracene upon application of 30,000 atmospheres. Development of technology for studying extremely high pressures at very low and very high temperatures and for observing reactions on the picosecond time scale.

420. LIGAND INTERMEDIATES IN METAL-CATALYZED FISCHER-TROPSCH SYNTHESSES \$ 48,700 02-1
J. A. Gladysz - Department of Chemistry

The goal of this research project is the homogeneous preparation and chemical characterization of ligand types believed to be intermediate in the conversion of CO-H₂ gas mixtures (synthesis gas) to methane, methanol, and higher alkanes and ²alcohols. Targets include metal-formyl complexes (1), hydrido hydroxycarbene complexes (2), α -hydroxyalkyl complexes (3), and methylidene complexes (4). Metal-formyl complexes are being synthesized by trialkylborohydride attack upon a variety of metal carbonyl compounds. The possibility that ligand types 2 and 3 will be available by deblocking t-butyl ether precursors is being investigated. High-pressure carbonylation, protonation, and decarbonylation, are being explored as other routes to ligand types 1, 2, and 3, respectively.

421. MULTIHETEROMACROCYCLES THAT COMPLEX METAL IONS \$ 73,916 02-2
D. J. Cram - Department of Chemistry

Studies to design, synthesize and evaluate cyclic organic compounds that selectively complex metal salts and solubilize them in organic solvents. These cyclic organic ligands are applicable to procedures for separating metal salts by differential distributions between water and organic solvents containing the ligands. The organic compounds possess charged cavities that match the sizes and charges of the metal ions they are designed to encapsulate. Compounds that will differentiate between actinides, lanthanides and the other products of spent reactor fuels are being sought.

UNIVERSITY OF CALIFORNIA/SANTA BARBARA (Continued)

427. HOMOGENEOUS CATALYSIS OF THE \$ 60,150 02-1
 WATER GAS SHIFT REACTION
 P. C. Ford - Department
 of Chemistry

Homogeneous catalysts for the water gas shift reaction are being investigated. Short term goals include better characterization of active species and reaction mechanisms for the ruthenium carbonyl system recently discovered to be an active homogeneous catalyst for the shift reaction. Longer term goals include investigations of other transition metal carbonyl systems for activity and the optimization of active systems for testing as supported liquid phase catalysts in a fixed bed flow reactor. Initial studies focus on metal carbonyl complexes, in particular metal cluster complexes, as possible catalyst candidates. Characterizing the fundamental chemistry involved in the activation of ligands such as carbon monoxide coordinated to mononuclear and polynuclear metal complexes provides a better basis for the logical design of other metal complex catalysts.

428. TRANSPORT AND REACTION IN \$ 33,613 02-4
 SUPPORTED LIQUIDS
 R. G. Rinker - Department of
 Chemical and Nuclear Engineering

The main objective of this research is to learn how to predict with reasonable confidence the effectiveness of supported liquid-phase catalysts (SLPC). Of particular interest are homogeneous organometallic catalysts, including cluster metal catalysts, dissolved in nonvolatile liquids which in turn are supported ideally as thin films on the pore walls of porous solids. The transport can then be coupled with a material balance to predict optimal loading as well as the effectiveness of SLPC. The test reaction chosen for confirming the theoretical developments is the valence isomerization of quadricyclene to norbornadiene (C_7H_8) using cobalt tetraphenylporphyrin dissolved in 1-chloronaphthene as the catalyst and supported in macroporous α -alumina pellets. Others under investigation include the water-gas shift reaction between carbon monoxide and water vapor to produce hydrogen at low temperatures (less than 200 °C) using a mononuclear or polynuclear organometallic catalyst or combinations of the two.

UNIVERSITY OF CALIFORNIA/SANTA CRUZ

429. PHOTOINDUCED ELECTRON TRANSFER \$ 38,029 01-1
 IN MIXED ORGANIC-INORGANIC SYSTEMS
 G. S. Hammond - Department
 of Chemistry

Study centers on photochemically induced electron transfer reactions of inorganic and organometallic substances. Ultimately the work may lead to means for screening and developing useful new photogalvanic systems.

UNIVERSITY OF CHICAGO (Continued)

433. BASIC STUDIES OF ATOMIC DYNAMICS
U. Fano - Department
of Chemistry
- \$ 86,917
- 01-3

This project supports studies designed to unravel the correlations between the motions of different particles and the energy exchanges between different types of motion in electron collision and photoabsorption processes. The effort is being directed toward achieving two distinct substantial advances on the theory of joint excitation and correlations of an electron pair. Other sustained efforts are directed to the application of atomic points of view to solid state problems and to the elucidation of the mechanism of atomic orientation by collision.

434. SYNTHESIS, CHEMISTRY AND CATALYTIC ACTIVITY OF COMPLEXES OF LANTHANIDE AND ACTINIDE METALS IN UNUSUAL OXIDATION STATES AND COORDINATION ENVIRONMENTS
W. J. Evans - Department
of Chemistry
- \$ 45,000
- 02-1

The objective of this investigation is the synthesis of several new classes of lanthanide and actinide complexes which should be instrumental in developing a more comprehensive understanding of the f orbital metals and which should participate in unusual catalytic transformations specific to these metals. The deliberately broad approach is designed to experimentally demonstrate a more extensive and practically important chemistry for the lanthanides and actinides than is presently known. The research is directed toward the synthesis of low and zero valent metal complexes as a primary goal. The nonaqueous reductive chemistry of these metals is being examined in a rather comprehensive manner and basic information concerning the interaction of the lanthanide and actinide metals in a variety of oxidation states with ligands such as phosphines, arsines, cyanides, isonitriles, silyls, stannyls, and olefins is being obtained.

COLORADO STATE UNIVERSITY

435. PALLADIUM CATALYZED COUPLING \$ 60,000 02-1
REACTIONS: MECHANISM OF
REDUCTIVE ELIMINATION
J. K. Stille - Department
of Chemistry

The synthesis of isomeric dialkyl, diaryl and mixed alkylaryl palladium complexes containing different geometries and ligands is being investigated. The effect of ligands, complex geometry, electronic structure of the organic moiety, and added electron acceptors on the rates of decomposition are being carried out in order to afford mechanistic information and define the optimum conditions for this step in potential catalytic cycles. The stereochemistry attending the elimination and the detection of reactive intermediates is being probed to provide additional mechanistic information. In addition, these mechanistic probes are being brought to bear on the reductive elimination reaction taking place from palladium(IV) complexes and binuclear palladium complexes.

COLUMBIA UNIVERSITY

436. LASER ENHANCED CHEMICAL \$ 61,727 01-1
REACTION STUDIES
G. W. Flynn - Department
of Chemistry

A series of experiments is underway to probe the influence of vibrational energy on both unimolecular and bimolecular chemical reaction processes. This experimental work will investigate the CF_2HCl HCl elimination reaction, the laser driven valence isomerization of perfluoro-Dewar-benzene, the laser enhanced isomerization of 1,2-dideuteroethylene, and several bimolecular reactions involving the methyl halides, COF_2 , and other molecular systems. Vibrationally enhanced chemical reactions of these species can be studied provided the probability for chemical reaction is larger than the probability for vibration-translation/rotation deactivation. These studies emphasize the importance of controlling and monitoring energy transfer processes and laser parameters. Experiments of this type are of fundamental as well as practical interest in the development of an improved understanding of chemical reaction processes.

CORNELL UNIVERSITY

437. HYDROGEN CYANIDE REACTIONS \$ 41,860 01-2
IN COMBUSTION SYSTEMS
W. J. McLean - Sibley School of
Mechanical and Aerospace Engineering

This research project is concerned with chemical processes associated with HCN in combustion environments. The objective of the research is to determine the rates and mechanisms of those reactions responsible for the formation of HCN and its subsequent conversion to other undesirable compounds. The experimental techniques employed in these studies involve the use of the single pulse (chemical) shock tube with quenched product analysis by gas chromatography, and the use of a high temperature fast flow reactor with product analysis by quadrupole mass spectrometry. Both of these techniques will be used to span a wide range of reaction times and temperatures, and the measured compositions will be compared with predictions based on plausible reaction mechanisms for HCN. In this coupling of experiment and chemical kinetic modeling we will be able to elucidate the important reactions involved with the behavior of HCN in combustion systems.

438. ESR STUDIES OF SURFACE \$ 90,000 02-1
ADSORPTION AND CATALYSIS
UNDER UHV CONDITIONS
J. H. Freed - Department
of Chemistry

The objective of this research is to develop and exploit a new approach for the study of surface adsorption and catalysis on clean metallic and oxide surfaces by ESR spectroscopy. In the experimental design, the microwave cavity is part of a ultra-high vacuum system so clean metallic surfaces can be prepared by vacuum evaporation onto the interior of the cavity walls. Various clean gases are directly adsorbed onto the surface and in situ ESR spectra obtained to study paramagnetic adsorbates and surface reaction kinetics. Studying these same clean surfaces with established techniques, makes it possible to directly interrelate the findings of the ESR experiments with those from these other methods.

UNIVERSITY OF GEORGIA (Continued)

446. A STUDY OF MECHANISMS OF HYDROGEN DIFFUSION IN SEPARATION DEVICES \$ 52,077 02-2
M. H. Lee - Department of Physics and Astronomy

Quantum mechanical formulation of the diffusion of hydrogen through palladium in order to ascertain if the failure of the classical treatment is due to the large difference in mass between the hydrogen and palladium atoms.

447. FUNDAMENTAL STUDIES OF SEPARATION PROCESSES \$ 62,000 02-2
L. B. Rogers - Department of Chemistry

Investigation of chromatographic systems at elevated temperatures and pressures; faster chromatographic methods for separating large molecules (polymers); determination of conditions for isolating vanadium impurities in petroleum crudes (catalyst poison in cracking and reforming operations). Investigation of factors that control the formation rate of deposits in geothermal brine heat exchangers.

GEORGIA INSTITUTE OF TECHNOLOGY

448. A KINETIC STUDY OF RADICAL-AROMATIC HYDROCARBON REACTIONS \$ 44,800 01-2
A. R. Ravishankara, F. P. Tully - Energy and Environmental Analysis Division, Applied Sciences Laboratory

This research program involves kinetic and mechanistic investigations of radical-aromatic hydrocarbon reactions of importance to optimization of energy production from alternative fuel sources. 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 $O(OH,H) + \text{aromatic hydrocarbons}$ will be made as functions of temperature and, when appropriate, pressure. Particular reaction pathways in the above processes will be 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.

UNIVERSITY OF ILLINOIS/CHICAGO CIRCLE

452. MEASUREMENT OF GAS PHASE REACTION RATES \$ 38,000 01-2
R. J. Gordon - Department of Chemistry

Study of hydrogen atom exchange reactions, $D + HX \rightarrow H + DX$ using flash photolysis with resonance fluorescence and laser absorption detection. The effect of vibrational excitation of HX on the reaction rate will also be studied. Study of the reaction of NO with ozone.

453. LASER-SCHLIEREN SHOCK TUBE STUDIES OF HIGH TEMPERATURE HYDROCARBON PYROLYSIS \$ 41,700 01-2
J. H. Kiefer - Department of Energy Engineering

The narrow-beam, laser-schlieren technique of Kiefer and Lutz will be used to investigate the early density gradient in full hydrocarbon (ethane, propane, butane, etc.) pyrolysis which is a direct measure of the rate of enthalpy change in these or any other endothermic process. The very earliest gradient (1 μ sec postshock) gives a quite unambiguous measure of the primary dissociation rate, and the later gradient can be used to extract secondary rates as well. The analysis will involve detailed computer modelling of the decomposition so that the (expectedly minor) influence of fast secondary reactions on the initial gradient can be included. Investigation of several fuel hydrocarbons is particularly useful for the determination of secondary rates, since their decomposition often involves the same secondary reactions occurring at different stages in the overall reaction.

ILLINOIS INSTITUTE OF TECHNOLOGY

454. STUDIES OF COMBUSTION KINETICS AND MECHANISMS \$100,000. 01-2
D. Gutman - Department of Chemistry

The object of this research is to develop a new method of generating polyatomic free radicals under controlled conditions which are important in combustion processes, and to use the new method to quantitatively study their important combustion reactions. The initial reactions to be studied all involve alkoxy radicals. These studies will provide the first direct measurement of the reactivity of these free radicals. The precursors to be used are nitrites, nitrates, and peroxides which will decompose by multi-photon absorption of the CO_2 laser pulses. Procedures for generating alkyl, acyl, sulfur-containing, and aromatic free radicals for later quantitative study are also being explored.

UNIVERSITY OF IOWA

455. DISTRIBUTION OF ENERGY IN \$ 44,000 01-1
BIMOLECULAR CHEMILUMINESCENT
REACTIONS
W. C. Stwalley - Department
of Chemistry

Study of chemiluminescent reactions involving hydrogen atoms; light emitted observed under high vacuum conditions; result of single (rather than multiple) collisions; wavelength analysis allows one to infer the molecule which emitted the light and the condition of its energy (i.e., the amount of energy tied up in the vibration and the rotation of its atoms and the amount tied up in chemically bonding electrons). A unique 25,000°K intense source of fast hydrogen (H) atoms has been developed and characterized to provide hydrogen atoms with various high velocities. Collisions of these fast H atoms with lithium (Li, Li₂ and Li-coated surfaces) have been observed to produce light throughout the visible region. Species emitting the light include high energy states of Li atom and of the molecules Li₂ and LiH.

JOHN HOPKINS UNIVERSITY

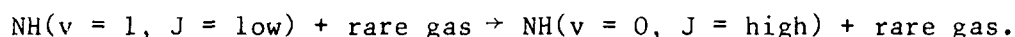
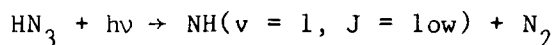
456. STUDIES IN HOT ATOM AND \$ 60,000 01-1
RADIATION CHEMISTRY
W. S. Koski - Department
of Chemistry

The energy and angular distribution of the reactions of B⁺ and Br⁺ with molecular hydrogen are being studied for the ground and the first excited electronic states of the projectile ions. By means of careful measurements of the limiting values of the translational exoergities we expect to be able to determine the product ion electronic states in the reactions. Attempts are being made to determine the contributions of the three J states, i.e., J=0, 1 and 2 of the ground electronic state of Br⁺ to the reactive scattering of the system. In continuation of work on the product ion internal energy distribution, the vibrational energy distribution of the reaction D (HD,D)D₂ is being examined. Another alternative reaction that is also being given attention is Si (H₂,H)SiH⁺. This latter reaction has a number of properties similar to the corresponding C⁺ reaction for which we were successful in determining the internal energy distribution of the CH⁺ product.

JOHN HOPKINS UNIVERSITY (Continued)

457. FAR INFRARED CHEMICAL LASERS \$ 61,115 01-1
D. W. Robinson - Department of Chemistry

The investigation of chemically-pumped far infrared lasers is continuing. There are two types: pure rotational, in this case diatomic OH, OD, and NH and vibrotational, specifically HCN [(010) \rightarrow (040)]. The reaction being studied in the diatomic case is,



Preliminary experiments on NH show laser action in three different electronic states as evidenced by the measured rotational constants of the emitting molecules. The triplet molecules, which require a collisional singlet-triplet conversion, are favored by the heavier rare gases. Identification of the states by more careful spectroscopic measurements, and pressure dependence studies are being made for the purpose of probing the kinetics and energy transfer rates. This is a remarkable system wherein pure rotational lasing apparently occurs in states with lifetimes reportedly short compared to the vibration-to-rotation transfer rates. The famous 300 μm laser emission of HCN, well-known from electrical discharge tubes, has been pumped chemically with the $\text{CN} + \text{H}_2$ reaction. There is an "incubation period" in the output and some other peculiar properties of the emission pulse. Sufficient intensity for the study of this laser has only recently been obtained, but now the pumping kinetics should be accessible through experimental manipulation of reaction conditions. The purpose here, besides the scientific goals, is to try to discern the practical limitations to the power of this laser. It was originally hoped that the discharge was inefficient for the generation, and destructive of HCN molecules, and that chemical generation might be far superior. Although the latter has not proved to be the case as yet, the reason is still unknown.

UNIVERSITY OF KANSAS

458. STEREOELECTRONIC PROPERTIES \$ 75,000 01-1
OF AGGREGATED CHLOROPHYLL
SYSTEMS
R. E. Christoffersen, G. M. Maggiora -
Department of Chemistry

Quantum mechanical and empirical potential function techniques will be employed in a comprehensive investigation of the electronic and geometric structure of a variety of molecular systems of importance in photosynthetic energy conversion. Quantum mechanical studies will include the completion of ab initio configuration interaction calculations already in progress on the low-lying singlet and triplet states of ethyl pheophorbide a and ethyl chlorophyllide a, and preliminary calculations on the related systems of bacteriochlorin, bacteriopheophorbide, and their magnesium containing analogs. Empirical potential function studies will include conformational analyses and determination of possible hydration or nucleophile binding sites of monomeric chlorophyll-type systems, and preliminary studies on dimeric systems. Finally, an assessment of the adequacy of currently utilized methods and, where appropriate, development of new or refined procedures to deal with large molecular systems (e.g. basis set generalizations and electronic structure and properties of chlorophyll cation and anion radical states) will be undertaken.

KANSAS STATE UNIVERSITY

459. ATOMIC PHYSICS WITH \$398,000 01-3
HIGHLY IONIZED IONS
J. R. Macdonald, P. Richard -
Department of Physics

This atomic physics accelerator research program is concentrated on understanding energy transfer and radiation loss due to highly charged ions that simulate heavy atom contaminants expected in high temperature energy producing devices (e.g. fusion energy). Highly ionized ions are produced in a controlled manner by use of the accelerator in order to independently measure the effects of electron capture at different atomic velocities and for known but different atomic configurations. Theoretical models are being developed to properly describe the electron capture and the subsequent radiation loss by the heavy atoms. This research on energetic highly ionized ions is performed under the five categories: (1) the production of x-rays in solid media, (2) the process of electron loss and gain in gas media, (3) x-ray spectroscopy in ion-atom collisions, (4) atomic collision theory and (5) applications and developments with heavy ion beams. The process of electron capture is studied experimentally and theoretically under categories 1, 2, 3, and 4. Alignment of atomic states is investigated through the observation of target and projectile radiation. Studies of the target thickness dependence of x-ray yields are designed to obtain target and projectile vacancy production and vacancy quenching cross sections in solids. X-ray spectroscopy of heavy ions will be initiated for x-rays with energy $\geq 4\text{keV}$ using a new Cauchois spectrometer. Impact parameter dependences of cross sections will be extended to heavier ion partners. This work provides a data bank of basic atomic physics describing the probability for radiation loss to take place.

LOUISIANA STATE UNIVERSITY

460. THEORETICAL STUDIES OF EXCESS \$ 36,365 01-1
ELECTRONS IN FLUIDS
N. R. Kestner - Department
of Chemistry

Theoretical studies and formulation of models for trapped electrons in various fluids as well as the study of electron transfer reactions. The studies of electrons trapped in polar fluids and fused salts have been carried out using model calculations as well as ab initio methods and the results compared with experimental data. Electron transfer reactions with special attention to their temperature dependence have been studied via multiphonon theory. Many examples of very weak temperature dependence have been predicted.

461. ELECTRON EXCITATION CROSS \$ 54,000 01-3
SECTIONS FOR MULTIPLY
CHARGED IONS
R. J. W. Henry, J. Callaway -
Department of Physics and Astronomy

This effort is the continuation of theoretical calculations of the cross sections for excitation of positive ions of the lithium and helium isoelectronic sequences by electron impact. The energy range considered extends from the threshold for excitation to approximately 4 times the ionization energy. The calculations are based on a close coupling expansion with exchange. Different methods of solution of the coupled integro-differential equations including the R-matrix method, the matrix variational method, and the non-iterative integral equation method are investigated for speed and accuracy. The energy range studied is one in which simple approximations of the Coulomb Born type are not valid. The contribution of Rydberg series of resonances below some excitation thresholds is to be determined. Extrapolation of excitation cross sections along the helium-isoelectronic sequence is to be made. Consideration of relativistic effects in both the structure of the ion and in the description of scattering as the nuclear charge increases will be made so that excitation cross sections for highly stripped impurity ions in high temperature plasmas of interest in thermonuclear reactors can be determined.

UNIVERSITY OF MASSACHUSETTS

465. DYNAMICS OF, AND HEAT AND MASS \$ 40,000 02-3
TRANSFER IN, AN INDUCTION
PLASMA
R. M. Barnes - Department
of Chemistry

Steady state solution of the fluid dynamics, transport of heat and mass and the particle dynamics of an induction plasma by formulating the solution from the general equations of transport of momentum, energy and mass and the Maxwell's equation of electromagnetic induction.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

466. PHOTOCHEMICAL ENERGY STORAGE \$ 81,412 01-1
STUDIES OF INORGANIC
PHOTOASSISTANCE AGENTS
M. S. Wrighton - Department
of Chemistry

This research involves the use of semiconducting solids as photoassistance agents for redox reactions involved in converting light to chemical and/or electrical energy. Specific materials under study are Si and Ge semiconductors which have been derivatized with electroactive groups for use as mediators for electron transfer reactions and to passivate the Si and Ge to photoinduced corrosion processes. Exploration of new interfacial photoredox reactions is being undertaken to assess the scope of such photochemical transformations. A Si-based photoelectrochemical cell has been demonstrated to sustain the conversion of light to electricity. The key find was that ferrocene in solution could be used to capture photogenerated holes before they could participate in destructive reaction to corrode the Si surface. Such results prompted experiments to attach electroactive ferrocene derivatives to the surface for the purpose of passivation and mediation of other oxidation reactions.

467. THEORY OF CHEMICAL KINETICS \$ 66,000 01-2
J. Ross - Department
of Chemistry

Research in the theory of chemical kinetics is in progress in chemical dynamics and chemical instabilities. The application of Franck-Condon factors has proven useful and we are studying thereby reactions with activation energies, the problem of vibration-translation transfer, the relation of such techniques to semi-classical methods, the effect of variation of initial excitation of reactants on reaction probability, and the connectivity of angular and energy distributions of reaction products. We propose to study unimolecular reactions by stochastic techniques in which transitions between energy levels of a dissociating molecule are possible and no restrictions of nearest-neighbor transitions are imposed. In the area of chemical instabilities we plan to study the kinetics of first-order phase transitions and the formation of macroscopic spatial structures as well as cooperative instabilities in the growth of colloidal and aerosol particles.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY (Continued)

468. PHOTOIONIZATION AND FIELD IONIZATION OF HIGHLY EXCITED ONE- AND TWO-ELECTRON ATOMS
D. Kleppner - Department of Physics
- \$ 75 000
- 01-3

Experimental and theoretical study of the interaction of highly excited atoms in applied static and oscillating electric fields. Studies include: systematics of field ionization, effects of symmetry-breaking interactions, relations between field ionization and autoionization, nonadiabatic effects in time varying fields, properties of planetary (doubly excited) atoms in strong fields, photoionization in Coulombic and non-Coulombic potentials, the structure of continuum states in applied fields, the characterization of field ionization for spectroscopy and other applications.

469. THE REDUCTION OF CARBON MONOXIDE BY EARLY TRANSITION METALS
R. R. Schrock - Department of Chemistry
- \$ 60,000
- 02-1

The primary objective of this research is to understand the organometallic chemistry of carbon monoxide reduction by the early transition metals. There is also interest in catalyzing reactions of small molecules such as olefins, acetylenes, and molecular hydrogen (in addition to carbon monoxide) to give larger more complex organic molecules with specificity at moderate temperatures and pressures. Specific studies include: (1) the preparation of Nb(III) and Ta(III) metal carbonyls, particularly those with less than 18 valence electrons (or with labile ligands) and a study of their reactions with H_2 , nucleophiles or electrophiles; (2) a study of reactions of CO with Nb(V) and Ta(V) alkyls as models for similar reactions with analogous hydrides; (3) the preparation of the related metal hydride complexes and a study of how they react with CO; and (4) the development of a bimetallic system which will "pull" CO apart or make it more susceptible to reduction by hydride ligands or controlled coupling to another CO.

MICHIGAN STATE UNIVERSITY

470. ELECTRON SPIN RESONANCE STUDIES \$ 40,000 01-1
OF RADIATION EFFECTS
M. T. Rogers - Department
of Chemistry

Paramagnetic fragments or defects produced by γ -rays, x-rays and ultraviolet light radiation damage in various classes of organic and inorganic solids are identified by their electron spin resonance (ESR) spectra. The measured ESR parameters are used to determine the electronic and molecular structures of the radicals. From the temperature and time dependence of the ESR spectra the stability of the radicals, their structural and conformational changes, and their chemical reactions are determined. Detailed studies are being made of several types of paramagnetic species which are interesting structurally but cannot be prepared in macroscopic quantities. Quantum chemical calculations of radical and transition metal complex geometries electron distributions are made. Organic materials currently being investigated include halocarbon derivatives, alicyclic compounds and unsaturated halocarbons. Inorganic materials being studied include fluoro- and chlorometallates, cyanides, and ions with unusual valence states; also hole species and excess-electron radicals. The ability to predict the nature of non-metallic materials is being developed.

UNIVERSITY OF MINNESOTA

471. STUDIES IN CHEMICAL \$ 50,907 01-1
REACTIVITY
R. W. Carr, Jr. - Department of
Chemical Engineering and Materials Science

A method of sensitivity analysis of coupled systems of ordinary differential equations is being extended to systems of partial differential equations. This allows sensitivity analysis of mathematical models of polluted atmospheres based on the continuity equation, and identifies the most important source terms for pollution. Sensitivity analysis is also used to assess models for atmospheric diffusion and reaction of chlorofluorocarbons. The effect of uncertainties in model input parameters is being assessed. Discrepancies in predicted atmospheric hydroxyl radical concentrations are being investigated. One-dimensional models of diffusion and reaction are being attempted for comparison with measurements of selected atmospheric constituents in an attempt to resolve the discrepancies. An experimental study of the reaction of CFCl_2 and CF_2Cl radicals with O_2 is being done. The reaction of these radicals² with O_2 plays an important role in the stratospheric release of chlorine from chlorofluoromethanes, as well as in directing the environmental fate of chlorine and fluorine following the tropospheric H-atom transfer reaction of OH with CHFCl_2 and CHF_2Cl . Investigations of methylene chemistry are being continued. Further experiments designed to detect $\text{CH}_2(^1\text{B}_1) \rightarrow \text{CH}_2(^1\text{A}_1)$ emission are being done, since these can provide information on the energy difference between the $\text{CH}_2(^1\text{A}_1)$ and $\text{CH}_2(^3\text{B}_1)$. Experiments on the kinetics and mechanisms of methylene reactions are being done by flash photolysis with time-resolved mass spectrometry.

UNIVERSITY OF MINNESOTA (Continued)

472. CONTRIBUTION OF ELECTRONICALLY EXCITED STATES TO RADIATION CHEMISTRY OF ORGANIC SYSTEMS \$ 75,000 01-1
S. Lipsky - Department of Chemistry

Absorption and emission spectra of low-lying molecular Rydberg states are being studied as a function of density of an external perturber in order to elucidate the origin of different sensitivities to perturbation of these two transitions between the same electronic states. The spectral shifts of Rydberg states caused by external molecular perturbation are being measured to obtain data for determination of the perturber liquid phase V_0 value. Electron-impact spectra are being compiled for a series of saturated, mono-olefinic and aromatic hydrocarbons at 0° and 90° scattering angles in order to reveal the presence of low-lying Rydberg transitions and to seek explanation for a peculiar enhancement in 90° spectra of high energy-loss transitions. Further evidence is being sought for the involvement of metastable Rydberg states in the photoionization process of a solute in a condensed phase by study of the action of scavengers and the effect of electric field strength on the fluorescence of the solute for excitation energies above and below the photoionization threshold. The S_3 , S_2 and S_1 emissions of p-xylene, toluene and benzene are being measured as a function of excitation energy and concentration of quencher in order to elucidate the mechanism of radiationless conversion of electronic energy in these molecules and the possible involvement in this mechanism of high-lying metastable states. Using a two-photon laser excitation process, a search will begin for the heretofore unobserved emissions from ethylene, methane, ethane and propane.

473. REACTION OF IONS WITH ATOMIC AND MOLECULAR FREE RADICALS \$ 45,000 01-2
W. R. Gentry - Department of Chemistry

Studies of the microscopic reaction dynamics in collisions of ions with atomic and molecular free radicals are underway in order to provide further fundamental information on the importance of electronic nonadiabaticity in chemical reactions. Work has focused on the reaction, $H_2^+ + B \rightarrow BH_2^+ + H$, to complement our previous studies of similar reactions in the $H_2^+ + C, N, O, F$ systems. Studies will be undertaken of reactions of the type $XH^+(X) + Y(YH) \rightarrow XY^+ + H$ where X and Y are first-row open-shell atoms. Data will be acquired over the range of relative kinetic energy from ~ 0.002 eV to > 20 eV, using a merged molecular beam apparatus.

UNIVERSITY OF MINNESOTA (Continued)

474. CONTINUOUS CHEMICAL REACTION CHROMATOGRAPHY \$ 30,000 02-2
R. Aris, R. W. Carr, Jr. - Department
of Chemical Engineering and Materials Science

Investigation of a chromatographic reactor with superior product yields and continuous operation; achievement of enhanced chemical reaction yields by chromatographic separation of the products and reactants; demonstration of continuous gas chromatography with radial flow in a rotating disc; combination of convection and adsorption in design, construction, and testing of a reactor to test predictions of the theory using reactions favored by chromatographic conditions.

475. STUDIES OF PHOTO-INDUCED CATAPHORETIC ISOTOPE SEPARATION \$ 73,250 02-2
H. J. Oskam, J. A. Carruthers,
L. M. Chanin - Department of
Electrical Engineering

Experimental investigation of isotope separation feasibility by a radiation-induced cataphoretic segregation process in gaseous discharges; resonance excitation and subsequent ionization by electrons; separation measurement of neon isotopes using a neon 0.63 μ laser and mercury isotopes using monoisotopic resonance lamps; light-spectrometer techniques.

UNIVERSITY OF MISSISSIPPI

476. THE RADIATION CHEMISTRY OF LIQUID AND PLASTIC CRYSTALS \$ 35,000 01-1
T. J. Klingen - Department
of Chemistry

The purpose of this investigation is the understanding of the radiation chemistry of compounds in the nematic liquid crystal state and of compounds in the plastic crystal state. From the understanding of the radiation chemistry in these mesomorphic states, it is the intention of this study to develop a model or models to explain the effects of radiation. Due to the liquid-like nature of these mesomorphic states, the initial effort is directed to a modified diffusional model. In addition to the standard radiation chemical approach to this problem, several other approaches are being made. One of these involves determination of the rotational energy barriers from polarized optical transmission spectra. The second involves determination of the diffusional barriers from nmr $T_1(\rho)$ measurements. The third approach involves determination of the initial G-values and nature of the species initiating the reactions from positron probe lifetime studies.

UNIVERSITY OF MISSOURI/ST. LOUIS

477. OBSERVATION OF LUMINESCENT SPECTRA IN LOW ENERGY ION-NEUTRAL COLLISIONS \$ 55,000 01-2
J. J. Leventhal - Department of Physics

The objective of these experiments is to obtain detailed information on the internal excitation energy of atoms and molecules after undergoing nonviolent (low energy) collisions. The experiments are performed by spectral analysis of the light emitted by the atoms and molecules following collision. From these spectra microscopic details of the collision mechanism can be determined; that is, the amount of energy stored in the molecular collision products as well as the partitioning of energy among the available internal energy levels. Subsequent studies will concentrate on collisions in which one of the colliding species is laser excited to a specific internal energy state. Collisions of this type are, in some cases, expected to react in a highly selective fashion and have been mentioned as a possible method of isotope separation.

UNIVERSITY OF NEBRASKA/LINCOLN

478. PRINCIPAL PROCESSES IN THE RADIOLYSIS OF GASES WITH FISSION RECOILS AND GAMMA RAYS \$ 80,000 01-1
G. G. Meisels - Department of Chemistry

The objectives are four-fold: to elucidate temperature and initial radical distribution in the fission recoil track and to measure the time involved between passage of the recoil and formation of the chemically reactive intermediate; to measure the rate constants for ion-molecule association reactions, the lifetimes of the intermediates, and the efficiency of displacements for the adduct; to assess the rates of intramolecular rearrangements of gaseous ions and its dependence on internal energy; and to investigate the structure of keragens in oil shales. In the first area, we employ competition kinetics involving reactions with different temperature dependencies and irradiate with recoiling fission fragments from a Pt clad, U 235-Pd foil over a range of gas pressures, with subsequent analysis by radio-gas chromatography. Mass spectrometric measurements employ a high pressure (1 torr) pulsed mass spectrometer capable of measuring ion residence times. A second mass spectrometer is based on the detection of photoelectrons with no kinetic energy and coincident measurement of ions produced in the same act to define the internal energy of the parent ion entirely. Application is primarily to simple hydrocarbon gases such as propane, methane, olefins, and to low boiling liquids such as methanol, acetaldehyde, etc., with suitable additives. Keragens are being analyzed using a high-resolution rapid scanning sensitive mass spectrometer (MS-50) using mild pyrolysis in the ion source itself.

UNIVERSITY OF NEBRASKA/LINCOLN (Continued)

479. HIGH ENERGY HALOGEN ATOM REACTIONS ACTIVATED BY NUCLEAR TRANSFORMATIONS \$ 41,838 01-1
 E. P. Rack - Department of Chemistry

Studies of high energy halogen atom or ion reactions, activated by various nuclear transformations in gaseous, high pressure and condensed phase saturated and unsaturated hydrocarbons, halomethanes and other organic systems are undertaken to better understand the mechanisms and dynamics of high energy monovalent species. Our experimental and theoretical program and its goals remain the same, consisting of six interrelated areas: (1) Systematics of high energy halogen reactions. (2) The reactions of iodine with olefins and acetylenes activated by radiative neutron capture and isomeric transition. (3) The gas to condensed state transition in halogen high energy chemistry. (4) Kinetic theory applications of high energy reactions and mathematical development of caging mechanisms. (5) The stereochemistry of ^{38}Cl and ^{128}I , $^{130}\text{I}^m + ^{130}\text{I}$ substitution reactions involving diastereomeric and enantiomeric molecules in the gas and condensed phase. (6) The applications of high energy chemistry techniques and theory to neutron activation analysis of biological systems.

480. CHARGE TRANSFER CROSS SECTION DETERMINATIONS IN HEAVY-ION - HEAVY-ION COLLISIONS \$ 35,000 01-3
 J. H. Macek, G. Gallup - Department of Physics and Astronomy

Total charge transfer cross sections are determined for the heavy ion reactions $A + A \rightarrow A^0 + A^{++}$ in two distinct parts: (1) Experimental measurements of the cross sections, using colliding beam techniques, are made for the cases where A is Xe, Cs, Ba, Au, Hg, and U. Initial measurements will be made for the center of mass energy range of 0-600 keV, with accuracies of $\pm 10\%$ or less. (2) Theoretical calculations of these reactions where A is Xe, Cs, and Ba are carried out. The major part of the theoretical work is directed toward calculating potential energy curves and wave-functions for the A^{++} systems. Once the molecular curves are calculated they will be used in a time dependent impact parameter treatment to calculate electron exchange cross sections. Theoretical support for the proposed measurements will be provided by calculating the cross sections for reaction $A^0 + A^{++} \rightarrow A^0 + A^{++}$ when A represents Xe, Cs or Ba. Extension to Au, Hg and U will require consideration of relativistic effects and the presence of f electrons.

UNIVERSITY OF NEBRASKA/LINCOLN (Continued)

481. PHOTOIONIZATION OF ATOMS \$ 67,800 01-3
 J. A. R. Samson, A. F. Starace -
 Department of Physics and Astronomy

The major objective of this experimental and theoretical research program is to unravel the effects of electron correlation and of spin-orbit interaction on atomic photoionization processes. Total and partial photoionization cross sections, photoelectron branching ratios and angular distributions, and multiple ionization cross sections, either over an energy region of a few Rydbergs above threshold or over the narrow energy region of an autoionizing resonance, will be measured and calculated by developing appropriate theory. These studies will be carried out both for the rare gases as well as for less studied atoms, in particular open-shell atoms. Among the atoms for which experimental work will be performed are the rare gases, metal vapors, and O. Among the atoms for which theoretical work is to be carried out are Al, Cl, and Xe. In addition, photoionization of hydrogen-like atoms in high magnetic fields will be studied.

UNIVERSITY OF NEVADA

482. TRIPLET ENERGY MIGRATION AND \$ 23,000 01-1
 TRANSFER IN LIQUIDS AND
 POLYMER FILMS
 R. D. Burkhart - Department
 of Chemistry

Optimizing rates of energy transfer in various materials; polymeric films; direct measurements of energy transfer rates in polymeric films; preferred directions of energy flow induced by mechanical orientation (stretching). Method for determining rates of migration of energetic molecules in fluid solutions; optical properties favorable for making measurements of energy migration rates; methods for producing uniform polymer films.

UNIVERSITY OF NEW MEXICO

483. ATOMIC PHYSICS WITH \$ 66,000 01-3
 RELATIVISTIC BEAMS
 H. C. Bryant - Department
 of Physics and Astronomy

Experimental studies to probe the structure of the simplest two-electron system (hydrogen minus) provide an important testing ground for atomic physics theories and calculational methods. Very large Doppler shifts allow continuously tuneable photon beams (1.5 to 20 eV) in the rest frame of 800 MeV hydrogen ions at the Los Alamos Meson Physics Facility (LAMPF). Single and double photodetachment measurements are made in the presence of strong (up to 5×10^7 volts/cm) electric fields. Stark multiplet structure and quenching are studied using polarized light. A survey of entire resonant region is to be made.

CITY UNIVERSITY OF NEW YORK/BROOKLYN COLLEGE

484. STABLE ISOTOPE STUDIES \$ 75,830 02-2
T. Ishida - Department
of Chemistry

Investigation of producing enriched isotopes efficiently and economically; isotope separation factors by reversible processes; correlation of molecular properties with isotope enrichment process efficiencies; measurement of low temperature vapor pressure differences of carbon-13 and -12 compounds; measurement of carbon isotope separation factors; optimization of the design and operation of isotope enrichment plants.

485. APPLICATION OF NUCLEAR AND \$ 51,018 02-3
RADIOCHEMICAL TECHNIQUES
IN CHEMICAL ANALYSIS
H. L. Finston, E. T. Williams -
Department of Chemistry

Determination of temperature effects on neutron capture cross sections for ^{22}Na ; Breit-Wigner parameters for ^{22}Na ; "Westcott" parameters for radioactive zirconium isotopes. Development of fast neutron activation analysis methods based on inelastic scattering and resonance capture; determination of elements in air samples by proton-induced x-ray fluorescence. Experimental reconciliation of acid-base theories; measurement of exchange currents to understand hydrogen overvoltage.

STATE UNIVERSITY OF NEW YORK/BUFFALO

486. STUDY OF DYE LASER INTRACAVITY \$ 49,749 01-2
ABSORPTION AS A DETECTOR OF
LOW DENSITY SPECIES
G. O. Brink - Department
of Physics and Astronomy

The technique of dye laser intracavity absorption (ICA) will be investigated as a possible tool for studying combustion processes. An ICA instrument will be constructed, then used in preliminary work to study low concentrations of atoms and molecules. Finally real combustion systems will be studied if the preliminary studies are successful.

NEW YORK UNIVERSITY

487. ENERGY RELATED ATOMIC AND MOLECULAR STRUCTURE AND SCATTERING STUDIES \$ 66,000 01-3
B. Bederson - Department of Physics

This is a program designed to study the basic properties and interactions of selected atoms and polar molecules using beam techniques. The program includes: (1) measurements of the electric dipole polarizabilities of alkali halide molecules, of their dimers and higher order clusters, (2) measurements of absolute total and differential cross sections for the scattering of low energy electrons by alkali halides, using the atomic beam recoil technique, (3) a study of methods for directly measuring hyperpolarizabilities and other atomic and molecular higher moments, using combined dc and laser fields, and (4) the eventual extension of cross section measurements to O, C, N, and U, and to other polar molecules such as KOH and H₂O. Methods for single particle detection of systems such as O, C, N and S are under study using laser excitation.

UNIVERSITY OF NORTH CAROLINA

488. ENERGY CONSERVATION BASED ON MOLECULAR EXCITED STATES \$ 51,167 01-1
T. J. Meyer - Department of Chemistry

Catalytic splitting of water into hydrogen and oxygen using visible light; related thermal processes for hydrogen and oxygen evolution; the development of photocatalysts for driving irreversible reactions in the non-spontaneous direction; and the development of photoelectrochemical cells based on excited state redox quenching. Work based mainly on polypyridine complexes of ruthenium including designed syntheses of new complexes having appropriate properties; studies of their thermal and photochemical reactivities; and the use of known, characterized excited states as chemical photocatalysts both in solution and in photoelectrochemical cells.

UNIVERSITY OF NORTH CAROLINA (Continued)

489. EXPERIMENTAL STUDIES OF ATOMIC INNER SHELL IONIZATION PHENOMENA \$ 56,047 01-3
S. M. Shafroth - Department
of Physics and Astronomy

The TUNL FN Tandem Van de Graff is providing beams of protons and heavy ions of several MeV/amu. Using these beams we are studying a variety of topics in inner shell ionization phenomena. When these beams impinge on thin-film solid or gaseous targets, they become highly ionized as do some target atoms. Much the same thing occurs in the case of impurity atoms in Tokamak fusion generators and in stars. It is interesting and valuable to study projectile and target energy-loss mechanisms by observing x-rays and electrons. We detect x-rays with semiconductor detectors or a curved crystal spectrometer, and soon plan to detect electrons with a parallel plate spectrometer. We are especially interested in target thickness effects on projectile and target x-ray production cross sections. Currently Cl^{n+} projectile x-rays are being examined under high resolution conditions when impinging on various targets to determine as nearly as possible the state of multiple ionization at the time of x-ray emission, lifetimes of metastable states, target thickness effects, and Doppler-shift effects on energies and line widths. Comparison of experimental zero impact parameter electron ejection probabilities with nonperturbative calculations of Merzbacher and students is encouraging.

NORTHWESTERN UNIVERSITY

490. THEORETICAL STUDIES ON HETEROGENEOUS COMBUSTION \$ 37,000 01-2
C. K. Law - Department of
Mechanical Engineering and
Astronautical Sciences

Study of the various heterogeneous processes occurring within vaporizing/combusting fuel sprays in the hot, oxidizing environments of various forms of liquid-fueled combustors. The approach is theoretical and will involve (1) the vaporization, ignition, deflagration, and extinction of individual fuel droplets in a reactive fuel/oxidizer environment; and (2) the vaporization of the droplet ensemble within a spray jet. The fundamental questions to be addressed are (1) the relative importance of premixed versus diffusional burning; (2) the relative importance of homogeneous versus heterogeneous burning; (3) the possible non-existence of the individual droplet combustion mode within the spray; and (4) the ignition and extinction criteria of the various droplet burning modes.

NORTHWESTERN UNIVERSITY (Continued)

491. THE PROPERTIES OF SUPPORTED METAL CATALYSTS \$106,000 02-1
J. B. Butt - Department of Chemical Engineering
R. L. Burwell - Department of Chemistry
J. B. Cohen - Department of Materials Science and Engineering

Chemical preparation of metal catalysts; detailed characterization of platinum, palladium, and rhodium catalyst particles and their alloys which are supported on alumina and silica; evaluation of catalytic properties by study of isotope exchange hydrogenolysis and hydrogenation reactions; elucidation of the role that the metal particle size and morphology play in determining catalytic properties.

492. SOLID STATE, SURFACE AND CATALYTIC STUDIES OF OXIDES \$ 84,345 02-1
H. H. Kung - Chemical Engineering Department
P. C. Stair - Department of Chemistry

The selective oxidative dehydrogenation of butene to butadiene on iron oxide catalysts is being studied in order to understand the roles of crystal structure and composition in the activity and selectivity of the oxide. Mixed metal oxides of iron of different crystal structures are being used to study geometric effects, substitution for iron by other metal ions is being compared to the iron spinel to study the effect of the nature of the transition metal ion. The oxides being investigated are chosen to isolate and study, as far as possible, one material property without interference from others. The experiments being carried out include: (1) the determination of surface composition of the metal oxides by Auger electron spectroscopy, (2) ultraviolet photoelectron spectroscopic study of butene adsorption, (3) adsorption and thermal desorption of NH_3 , CO_2 , butadiene and acrolein, and (4) isotope labelling and measurement of activity and selectivity in a pulse reactor. These experiments are chosen to study the surface composition and structure, and the interaction of the surface with reaction molecules. Correlations among the kinetic and static measurements are being sought.

OHIO STATE UNIVERSITY

493. PULSE RADIOLYSIS STUDIES OF FAST REACTIONS IN MOLECULAR SYSTEMS \$ 75,349 01-1
L. M. Dorfman - Department of Chemistry

The fast reaction kinetics of elementary processes in irradiated molecular systems are being studied by the pulse radiolysis technique. A principal interest of the current work is concerned with the properties and chemical behavior of molecular ionic species in organic liquids. The objective is the understanding of the mechanisms of chemical change in the systems selected, and the determination of the specific reactivity of the transient species which determine the chemistry. Ancillary to this objective is the observation of optical absorption spectra of the reactive transients. Detection by fast optical absorption measurement in the ultraviolet, visible and infrared regions is being used. Specific areas of current interest are: (1) Rates and mechanism of positive charge transport in organic liquids. (2) Effect of substitution on reactivity of carbonium ions. (3) Reactions of arylcarbenium ions with alkenes (initiation step in cationic polymerization). (4) Ion-pairing of carbocations and of carbanions. (5) Transient species in aquo-organic systems.

494. KINETICS OF IONIZING RADIATION INDUCED REACTIONS \$ 52,000 01-1
R. F. Firestone - Department of Chemistry

Elucidation of mechanisms for decay of excited rare gas atoms and for growth and decay of excited molecular species (excimers) in pure rare gas samples and in mixtures of rare gases with foreign molecules and atoms. Direct excitation of highly excited rare gas atoms and ions is effected by irradiation of rare gas samples with pulsed high energy electron beams. Formation of Paschen(1s) atoms occurs via radiative cascade. At pressures from ca. 100 to ca. 1000 torr. excimer species form predominantly via collisional mechanisms and decay via radiative transitions. Energy transfer from excited atoms and excited molecules to quenching agents as well as mechanisms for decay of excited atoms in pure rare gases will be examined in detail. All species are monitored by means of fast absorption spectrophotometry.

OREGON STATE UNIVERSITY

495. THERMAL-ENERGY SCATTERING OF ATOMS IN HIGH RYDBERG STATES \$ 50,987 01-3
C. A. Kocher - Department of Physics

Collision dynamics for thermal-energy encounters between long-lived highly excited Rydberg states and ground-state gaseous targets; atomic beam measurements of the angular and velocity dependence of differential cross sections; analysis of the relation of Rydberg state scattering to free-ion scattering at thermal energies.

UNIVERSITY OF PENNSYLVANIA

496. ANISOTROPIC INTERACTIONS AND ROTATIONAL ORDERING IN SOLIDS \$ 9,100 01-2
D. White - Department of Chemistry

This is an experimental and theoretical program concerned with anisotropic interactions in isotopic molecular crystals, order-disorder phenomena involving molecular orientations and low energy elementary excitations in such solids. The experimental results are used to establish relationships between isotopic effects and intermolecular forces which are important in the explanation of macroscopic and microscopic behavior of condensed phases as well as the energy transfer pathways. The research will focus on the studies of ortho-para mixtures of solid deuterium in the rotationally ordered phase.

497. THERMOCHEMICAL PROCESSES FOR HYDROGEN PRODUCTION BY WATER DECOMPOSITION \$110,000 02-4
D. Perlmutter - Department of Chemical Engineering

This research project is a continuation of work in progress on modeling and experimental tests in rotary chemical reactors. A model previously developed is to be extended to include thermal effects on conversion. Further modification of laboratory equipment will provide tests for scale-up procedures, and will expand the range of solids surveyed and catalysts used.

PENNSYLVANIA STATE UNIVERSITY

498. THE PHOTOCHEMICAL DECOMPOSITION § 72,526 01-1
OF DISILANE, PHOSPHINE AND ARSINE
F. W. Lampe - Department
of Chemistry

Studies of the elementary chemical reactions and overall chemical conversions brought about by the irradiation of gaseous silanes and germanes with gamma rays and vacuum ultraviolet light are being carried out: (1) Ion-molecule reactions characteristic of silane and germane systems are being studied in a tandem velocity filter-mass filter apparatus in which reactant ions of a given mass, with energies of 0.5-20 electron-volts, are focused into a target gas and the resulting product ions are analyzed with respect to both mass and energy. Particular attention is directed towards a study of the lifetimes, rates of unimolecular dissociation, and collisional stabilization of energy-rich collision complexes. The role of halide and hydride abstraction and bridging in ion-molecule reactions of silane-halocarbon and germane-halocarbon is also being studied. We shall also attempt in these studies to establish the existence of GeH_5^+ and measure its thermochemical properties. (2) The mechanisms of photochemical decomposition of silanes and germanes using 147 nanometer radiation are being studied in a photolysis cell that is directly coupled to a time-of-flight mass spectrometer. Particular attention is directed to the possibility of useful photochemical synthesis by the room-temperature reactions of divalent silylene and germylene radicals with substrates containing halogen and oxygen atoms and carbon-carbon double bonds. (3) The solid hydridic films of silicon and germanium that are formed in all decompositions of gaseous silanes and germanes are studied. The chemical nature of the films formed by gamma and vacuum ultraviolet irradiation, and by high intensity CO_2 laser irradiation, and dependence of this nature on reaction conditions particularly investigated. The semiconductor properties of the films and their dependence on reaction conditions is also being studied.

499. OSCILLATOR STRENGTHS FOR § 52,336 01-3
HIGHLY IONIZED ATOMIC SYSTEMS
C. F. Fischer - Department
of Computer Sciences

The effectiveness of the MCHF (Multi-centered Hartree-Fock) procedure for including not only correlation among outer electrons, but also core polarization effects in the determination of theoretical f-values was exploited. Spin-orbit interaction was included to extend the validity of a non-relativistic model to higher Z-values. Several $\Delta n = 0$ transitions in the Mg and Zn sequence were considered. Results including only outer correlation were compared with recently published fully relativistic values including fewer correlation effects. Several 3d - 4f transitions in the He and Al sequence were investigated. Though $\Delta n \neq 0$, the f-values were expected to be large. Continued research will result in ionization potential and f-value data for a series of states and ions, including elements present in Tokamak plasmas. A preliminary study will be made of the applicability of the MCHF procedure to theoretical determination of Auger transition rates. The MCHF method is likely to yield more accurate results than the Hartree-Fock-Slater method often used for this purpose.

PENNSYLVANIA STATE UNIVERSITY (Continued)

500. CRYSTALLITE SIZE AND SUPPORT \$ 88,061 02-1
INTERACTIONS ON CO HYDROGENATION
M. A. Vannice - Department
of Chemical Engineering

This research deals with the ultimate development of more effective catalysts for synthesizing hydrocarbons from H_2 and CO. One objective of the research is to understand the relationship between (1) the catalytic metal crystallite size and (2) metal-support interactions on the reactivity of the surface for the $H_2 + CO$ synthesis reactions. Of particular interest is the relationship between product selectivity and the CO adsorption bond strength. This work is relevant to methanation reactions; however, the emphasis is to minimize CH_4 formation and maximize the production of olefins and chemical intermediates.

UNIVERSITY OF PITTSBURGH

501. MICROWAVE-OPTICAL DOUBLE \$ 50,000 01-2
RESONANCE SPECTROSCOPY
D. W. Pratt - Department
of Chemistry

The principal objective of this research project is to develop basic knowledge about the structure of matter and its interaction with radiation through the exploration of new physical and chemical phenomena. Of particular interest are short-lived chemical species which are produced by irradiation of solids with x-rays, γ -rays, and ultraviolet light, and include electronically-excited molecules, free radicals, and collective excitation in solids. Because of their short lifetimes, the development of new experimental techniques such as optical detection of magnetic resonance spectroscopy forms an integral part of this project.

502. CHARGE-EXCHANGE COLLISIONS \$100,000 01-3
OF HIGHLY STRIPPED IONS
WITH ATOMIC HYDROGEN
J. E. Bayfield - Department
of Physics and Astronomy

Experimental studies are made of charge exchange processes involving highly stripped ions. The measurements are required to assess impurity radiation loss mechanisms and auxiliary neutral beam plasma heating effectiveness in magnetic fusion systems. The unique Pittsburgh double EN tandem accelerator-decelerator facility produces carbon, nitrogen and oxygen ion beams of every possible charge state (including totally stripped) with energies variable from 30 MeV to below 200 keV. The ion deceleration capability has been developed specifically for these experiments and is essential for studies with the totally-stripped and one-electron ions below 4 MeV. Data with these ions is particularly valuable for comparison with recent theoretical predictions.

PRINCETON UNIVERSITY

503. DYNAMICAL STUDIES OF \$ 51,358 01-2
MOLECULAR SYSTEMS

H. Rabitz - Department
of Chemistry

This research can be divided into two categories: (1) the theoretical treatment of individual molecular collision events, and (2) the analysis of macroscopic kinetic relaxation phenomena. Within each of these categories several projects are under way or will be initiated. The work in category (1) involves the development of practical means for reliably calculating collision information, detailed quantum mechanical calculations to ascertain the key molecular parameters controlling collision behavior, and the development of variationally derived interpolation schemes for extending available collision information. The raw collision information generated by these studies can be used to correlate and analyze experimental data. In this regard the work in category (2), research on kinetic relaxation phenomena, involves the sensitivity analysis of chemical kinetic mechanisms, the deconvolution of experimental relaxation data to yield state-to-state rate constants, and the analysis of highly non-equilibrium behavior in expanding gases. All aspects of the research utilize a variety of techniques, many of which are being developed.

504. SUPPORTED CATALYST \$ 90,000 02-1
SYNTHESIS AND CHARACTERIZATION

J. Turkevich - Department
of Chemistry

Development of supported catalysts for petroleum refining, chemical processing, and cleanup of automotive exhausts; synthesis of uniform-sized particles of platinum, palladium, and gold; adherence of catalysts on supports of uniform size and shape; characterization of catalysts in solution form by absorption spectroscopy, ultracentrifugation, light scattering, transmission electron microscopy, and in solid form by electron microscopy, gas chemisorption, poisoning of active centers and catalytic activity.

UNIVERSITY OF ROCHESTER

510. LOW ENERGY ION-MOLECULE REACTION DYNAMICS AND CHEMIIONIZATION KINETICS
J. M. Farrar - Department of Chemistry
- \$ 41,800
- 01-2

The work seeks to extend our knowledge of low-energy ion-molecule reaction dynamics by performing crossed-molecular beam studies. The systems chosen for study involve reactions of H_2^+ with CO, N_2 , O_2 , and F in which proton-transfer and charge-transfer reactions are expected to occur. The simplicity of the reactants suggests that reasonably accurate potential surfaces can be calculated and that the details of the reaction dynamics can be correlated with features of these potential surfaces. A second area of study concerns chemi-ionization reactions of free-radical species thought to be present in hydrocarbon flames. Attention is focused on reactions of CH radicals, among these the associative ionization reactions $O+CH \rightarrow HCO^+ + e^-$ and $CH + C_2H_2 \rightarrow C_2H_3^+ + e^-$. By measuring total cross sections for ion production as a function of relative collision energy, the nature of the coupling between the potential surfaces of the free-radical and associative ion can hopefully be elucidated. The energy distributions of the electrons emitted in the ionization reaction are being measured to probe the difference potential between these two surfaces. A molecular beam - mass spectrometer - electrostatic energy analyzer apparatus is being employed for these studies.

511. FUNDAMENTAL STUDIES IN ISOTOPE CHEMISTRY
J. Bigeleisen - Department of Chemistry
- \$ 95,000
- 02-2

Theoretical correlation of isotope effects with molecular and intermolecular forces; experimental investigation of condensed media. Study of quantum effects via isotope effects. Isotope fractionation in two component mixtures. Isotopic chemistry of carbon and oxygen related to molecular potential functions. New class of sum rules for molecular vibrations.

STANFORD UNIVERSITY (Continued)

516. FUNDAMENTAL STUDIES OF FLUID MECHANICS AND HEAT TRANSPORT IN POROUS MEDIA \$ 31,615 02-4
G. M. Homsy - Department of Chemical Engineering

Fundamental problems in flow and transport in porous media are being studied. The first problem is a mechanical description of the flow of non-Newtonian fluids through porous media. The objective is to develop a theory based upon retarded motion expansions for rheologically slow flow to provide a rational extension of Darcy's law to account for non-Newtonian effects. Predictions are tested by a series of experiments in which the response for flow through fixed beds is measured. It is also the objective to understand the stability of the displacement of a Newtonian fluid by a non-Newtonian fluid, a subject of interest for improved recovery of oil. Convection in porous media which is driven by temperature differences is studied with modern computational techniques to describe the flow which is known to bifurcate from steady two-dimensional flows.

SYRACUSE UNIVERSITY

517. MECHANISM OF GAS PERMEATION THROUGH POLYMERIC MEMBRANES \$ 46,419 02-2
S. A. Stern - Department of Chemical Engineering

Permeability coefficients are being predicted for selected penetrant polymer systems using parameters determined from high-pressure diffusivity measurements and a model based on "free-volume" concepts. The predictions will be compared with experiments in order to establish the regimes of validity of the model.

UNIVERSITY OF TENNESSEE

518. RESEARCH CONCERNING IONIC AND FREE RADICAL REACTIONS IN RADIATION CHEMISTRY
T. F. Williams - Department of Chemistry
- \$ 68,000 01-1

The objective of this work is to identify intermediates generated by the passage of radiation in liquids and solids and to understand the chemistry of the resulting highly reactive intermediates (ions and free radicals). The research is especially focused on paramagnetic intermediates possessing an unpaired electron since these species respond to detection by electron spin resonance (ESR) spectroscopy. In this way it is possible to detect and identify negative ions of fluorocarbons and other molecules formed by electron attachment to the parent molecule. An important aspect of this work is the demonstration of electron attachment to many so-called saturated molecules, the resulting hypervalent radical ions violating the octet rule of electron configuration in atoms and molecules. This research demonstrates the importance of quantum tunneling in hydrogen-atom transfer reactions at low temperatures. These reactions involving methyl radicals are characterized by very large deuterium isotope effects and they occur with almost zero activation energy below 40 K. This work will be extended to study the reactions of hydrogen atoms which are known to be highly selective under certain conditions at very low temperatures.

UNIVERSITY OF TEXAS

519. PHOTOEJECTION AT ELECTRODES AND ENERGY STORAGE BY CARBON-CARBON BOND FORMATION
M. A. Fox - Department of Chemistry
- \$ 38,113 01-1

This research is concerned with the evolution of a program devoted to developing a practical, viable system for using visible light photochemical reactions of organic compounds to store solar energy. Two approaches to this solar energy conversion include (1) organic photoelectrochemistry and (2) the use of visible light to prepare relatively strained or destabilized compounds which can subsequently exothermically revert to starting material. Basic research on experimentally controllable factors favoring photoinduced electron exchange at appropriate electrodes are being undertaken to determine conditions for optimal conversion of light to electrical energy. Pericyclic reactions of organic carbanions are being examined as methods to store light energy as chemical energy. Emphasis is placed on the chemical, photochemical, electrochemical and thermochemical interrelationships within a series of photoactive compounds. A study of the mechanism of photoinduced electron ejection from highly colored carbanions to semiconductor electrodes has been undertaken. The quantum efficiencies and achievable potentials from these processes are being measured. The dispersal of the photoactive molecules as monolayers or at chemically-modified (bound) electrode surfaces and the solvent significantly affect the efficiency of these sensitization processes. Photoinduced ring closure reactions in several pentadienyl anions are being explored as a method of storing solar energy in strained chemical bonds. New techniques for the formation of carbon-carbon bonds by visible light photolysis are being sought.

TEXAS A&M UNIVERSITY

520. HOT ATOM REACTIONS INVOLVING \$ 35,000 01-1
MULTIVALENT AND UNIVALENT SPECIES
Yi-Noo Tang - Department
of Chemistry

In the recent years we have studied the chemical reactions of high energy atoms of various elements formed by nuclear reactions via the use of either a nuclear reactor or a cyclotron. The energetic atoms under study include the radioactive isotopes of hydrogen (in the form of tritium), carbon, silicon and phosphorus. The last three are capable of forming more than one chemical bond to give stable products. In particular, we have studied the details of the interactions of these energetic atoms with highly unsaturated molecules possessing conjugated double bonds, that is, with alternate single and double bonds. The energetic atoms may either interact directly with such conjugated molecules to give an adduct which rearranges to give final products, or they may abstract atoms from other molecules to give species such as carbenes and silylenes and then interact with the conjugated systems. For example, Si atoms may abstract two H atoms to give silylene, SiH₂. The reactions of various silylenes have been studied in detail. The understanding of the reactions of the energetic atoms formed via nuclear reactions should be essential for the background knowledge and environmental consideration of both nuclear fission and nuclear fusion processes.

521. STORED-ION COLLISION \$ 49,500 01-3
MEASUREMENTS
D. A. Church - Department
of Physics

Magnetic and electric fields are used to confine charges in quadrupole structures. Resonant excitation and detection methods are employed to investigate, control and characterize the charged particle position and energy distributions. Initial research is directed towards development of techniques to measure reaction rates and cross sections of multi-charged-ion collision processes with both charged and neutral collision partners, e.g., atoms, molecules, photons, and electrons; and also to detect de-excitation radiation.

522. X-RAY EMISSION FROM MULTIPLY \$ 36,500 01-3
IONIZED ATOMS PRODUCED IN
HEAVY ION COLLISIONS
R. L. Watson - Department
of Chemistry and Cyclotron Institute

Investigation of chemical effects on K α x-ray satellite structure produced in heavy-ion-atom collisions, including the dependence on molecular structure, and on projectile energy and atomic number. High resolution x-ray spectroscopy of multiply ionized atoms. Study of the excitation and decay mechanisms of inner-shell vacancy states in both the target-atom and the projectile-ion collision partners with particular emphasis on level matching and line broadening effects. Characterization of surface interactions in beam-foil experiments by means of x-ray measurements.

TEXAS SOUTHERN UNIVERSITY

526. SOLVENT EXTRACTION STUDIES \$ 35,000 02-2
USING HIGH-MOLECULAR-WEIGHT
AMINES
C. W. McDonald - Department
of Chemistry

Methods to remove metal ions, especially toxic metals such as lead, cadmium, mercury, and chromium, from aqueous solutions via amine liquid-liquid extraction or surfactant-foam separation. Methods to be conservative of energy and economic, and amenable to scale-up for industrial use with waste water. Elucidation of associated chemistry.

UNIVERSITY OF UTAH

527. DYNAMICS AND MECHANISMS \$ 52,000 01-1
OF HOT ATOM CHEMISTRY
L. D. Spicer - Department
of Chemistry

Study of reaction kinetics, atomic and molecular collision dynamics, and energy transport at energies significantly above thermal thresholds. Intramolecular energy transfer following nuclear recoil chemical activation is being explored. The recoil chlorine atom replacement reaction in chloroalkylcyclopropanes is being used to activate the molecule. Decomposition of the cyclopropyl ring as a function of pressure and alkyl chain length are monitored to characterize the flow of energy within the molecule. Intermolecular energy transfer from nascent cyclobutane-t produced in the recoil hot tritium atom replacement reaction with cyclobutane is also being studied. Detailed comparison of the unimolecular behavior in various non-reactive bath gases is being made using an RRKM model with multistep collisional deactivation in order to determine the average quanta of energy transferred per collision in each bath gas. Kinetics and mechanisms of photochemical reactions between sulfur dioxide and saturated hydrocarbons are also being investigated.

UNIVERSITY OF UTAH (Continued)

528. COMBUSTION PROCESSES STUDIED \$ 45,000 01-2
BY INFRARED MULTIPHOTON
ABSORPTION
W. A. Guillory - Department
of Chemistry

The objective of this research is to use the phenomenon of infrared multi-photon absorption (IMA) to study elementary photophysical and photochemical processes related to flame and combustion systems. At collisionless pressures, IMA has recently been shown to be a statistical process, occurring almost exclusively in the vibrational degrees of freedom, resulting in what appears to be unimolecular dissociation from several surfaces of the ground electronic state. The focused radiation of a pulsed CO₂ TEA laser (70-250 nsec. FWHM) is being used to initiate these flame and combustion processes. This means of reaction initiation provides a significant and important advancement in time-resolution, so that mechanisms and energy distributions can be more effectively determined. Stable and unstable (free radicals) species generated will be monitored by wavelength and temporal-resolved spectroscopy using laser-induced fluorescence, resonance lamp induced fluorescence (atom detection), and infrared emission. Initial systems for study are methanol, ethylene, allene, propylene, propane, and propenal with and without the presence of oxidants.

529. ¹³C NMR AS A TOOL FOR THE \$ 94,708 02-1
ANALYSIS OF HYDROCARBON
MIXTURES
D. M. Grant, R. J. Pugmire -
Department of Chemistry

The objectives of this research are to explore and develop the capabilities of carbon-13 NMR techniques for the identification of molecular species in complex liquid mixtures derived from coal. Our approach is to use the unique features that carbon-13 NMR (cmr) has to offer in structure identification and elucidation; i.e., wide spectral dispersion, sensitivity to minor structural variations and conformational features, reproducible additivity effects which permit chemical shift parameterization, and sensitivity to isomeric structure of similar compounds. An archival file of chemical shift data on compounds which are known or are expected to be found in coal derived liquids is being established. Chemical shifts of compounds which are not presently in the literature which are needed in the archival file are being measured. Initial attention is being focused on hydroaromatic compounds known to be important in hydrogen transfer mechanisms associated with liquefaction and gasification processes. The conditions under which cmr techniques can be used quantitatively in complex hydrocarbon mixtures are being investigated. Existing techniques for computer assisted cmr spectral interpretation are being evaluated.

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

530. REACTIONS OF CHARGED AND NEUTRAL RECOIL PARTICLES FOLLOWING NUCLEAR TRANSFORMATIONS
 H. J. Ache - Department of Chemistry
- \$ 66,371 01-1

An important but still little understood field of fundamental chemical kinetics is the area that deals with those chemical reactions that occur above the threshold or activation energy. In this program translationally hot species (atoms or ions) are generated following nuclear reactions and their interactions with various substrates are studied in order to assess the reaction efficiencies as a function of the kinetic energies associated with the reactants. Specific studies of the reactions of energetic species generated in nuclear transformations are: (1) study of the nuclear decay induced reactions of halogen species with organic compounds. This investigation includes the evaluation of the reaction mechanisms leading to halogen for halogen (or hydrogen) exchange and the stereochemistry of these processes; (2) study of non-synthetic methods to incorporate radioactive nuclides into compounds of biological interest, e.g., by nuclear decay induced exchange; (3) study of the energetics, mechanisms and the exact nature (i.e., spin state, etc.) of the species involved in the reactions of energetic carbon-11 atoms with organic substrate molecules; (4) study of the crystallochemical reactivity of trapped recoil particles and implanted species; (5) study of the chemical consequences of Auger charging in biomolecules.

WASHINGTON UNIVERSITY

531. REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS
 P. P. Gaspar - Department of Chemistry
- \$ 59,000 01-1

Investigations of reactions of recoiling silicon and germanium atoms from $^{31}\text{P}(n,p)^{31}\text{Si}$, $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$, $^{76}\text{Ge}(n,2n)^{75}\text{Ge}$, and $^{74}\text{Ge}(n,\gamma)^{75}\text{Ge}$ with simple inorganic and organic substrates are being performed. Si and Ge atoms, ions and radicals produced chemically are also being studied and compared with recoil experiments. Goals of research are: What is the chemistry of recoiling Si and Ge atoms and how do reactions take place? What are the relationships among structure, energy and reactivity? The research program examines reaction products, determines reaction mechanisms. The focus is on primary steps in reactions of recoiling Si and Ge atoms, structure, energy and electronic states of reaction intermediates, role of ions in recoil reactions. Reaction sequences have been determined for recoiling silicon and germanium atoms. Intermediacy of divalent silicon and germanium radicals have been found important. Ion molecule reactions of Si^+ have been explored. Role of Si^+ in recoil reactions has been investigated. New thermal reactions of SiH_2^+ with unsaturated organics were found. New routes to GeR_2 have been developed.

WASHINGTON STATE UNIVERSITY

532. CATALYTIC OXIDATIONS USING \$ 83,000 02-1
TRANSITION METAL CARBONYL
CLUSTERS
D. M. Roundhill - Department
of Chemistry

There are two aspects to this research project. The first explores the use of transition metal carbonyl cluster compounds as homogeneous oxidation catalysts. Most of this work employs molecular oxygen as the oxidant and focuses on clusters which may provide selective control of free-radical autoxidation reactions. The second part involves kinetic and mechanistic studies on the reactivity of ligated dioxygen. The long range objectives of this research program are to aid in the development and understanding of homogeneous oxidation catalysts which can utilize molecular oxygen, are selective and energy efficient.

WAYNE STATE UNIVERSITY

533. RADIOLYSIS STUDIES ON \$ 94,000 01-1
REACTIVE INTERMEDIATES
L. Kevan - Department
of Chemistry

This research is oriented toward quantitative characterization of presolvated electron structure and reactivity, metal atom and ion solvation and radical and molecule orientation on surfaces. The geometrical and electronic structure of presolvated electrons formed at 1.5 and 4.2 K in aqueous and organic matrices are studied by electron spin resonance, optical absorption and photoconductivity methods. Metal atom solvation and radical orientation on zeolite surfaces are studied by electron spin echo spectrometry and other advanced electron spin resonance methods. Electron reactivity is being studied at temperatures below 4 K.

WAYNE STATE UNIVERSITY (Continued)

534. PHOTOCHEMICAL ACTIVATION AND REACTIVITY OF POLYNUCLEAR METAL COMPLEX MOLECULES \$ 50,000 01-1
R. L. Lintvedt, J. F. Endicott -
Department of Chemistry

This project involves study of the reactivity of photoexcited molecules containing two or more transition metal ions. There are two broad objectives that are pursued. One is to explore the photochemistry of binuclear coordination complexes with a view to discovering two electron processes or at least redox processes that avoid free radical intermediates. Another is to discover binuclear complexes from which useful reactive intermediates may be generated. It is a major concern to determine how the photochemical and thermal-chemical reactivity is mediated by the electronic structure of the metals and by interactions between the metal centers. The project deals with several binuclear complexes derived from 1,3,5-triketones and their Schiff-base derivatives, many of which have already been prepared and characterized in our laboratories. The series includes several different transition metal ions in both homobinuclear and heterobinuclear complexes. Our immediate goals are: (1) to synthesize binuclear complexes which are (a) strongly absorbing and likely to have long excited state lifetimes or (b) likely to form reactive, but metastable intermediates (e.g. hydrides); (2) to characterize photoredox processes in certain binuclear complexes; and (3) to characterize photophysical processes in similar complexes.

535. ELECTRONIC RELAXATION PROCESSES IN POLYATOMIC MOLECULES \$ 52,000 01-2
E. C. Lim - Department
of Chemistry

The main thrust of this research is to investigate isotope effects on electronic relaxation as a probe of detailed mechanisms of radiationless processes. Three studies are underway. The first involves study of isotope, viscosity, and temperature effects on the formation and decay dynamics of excimers and exciplexes. The specific question addressed is the role of the inter-ring stretching vibration in radiationless transitions of these systems. The second explores the isotope effects on both the overall and the spin sublevel decay rates of the lowest triplet state (T_1), and their dependence on the T_1-T_2 vibronic coupling. Many of the experiments are designed to test the specific theoretical predictions based on the important working hypothesis that the vibronic coupling between $n\pi^*$ and $\pi\pi^*$ states leads to a very efficient radiationless transition from the lower of the two vibronically coupled states (proximity effect). Finally, in the third study, we examine the lifetimes of triplet triplet fluorescence and their deuterium isotope effects in anthracene and its derivatives. This study will be combined with spectroscopic investigations of lower-lying triplet states to gain a detailed understanding of the mechanism of singlet triplet intersystem crossing in aromatic hydrocarbons.

UNIVERSITY OF WISCONSIN

536. STUDIES IN HOT ATOM AND RADIATION CHEMISTRY \$ 88,547 01-1
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 by ionizing radiation, by photolysis, and by metal photosensitization. The reactions under study are initiated by irradiation with gamma rays from ⁶⁰Co; and by ultraviolet, visible and infrared radiation from continuous sources, flash sources and a tunable laser. Electron spin resonance, infrared, visible, ultraviolet and mass spectrometry, gas chromatography, electrical conductivity, luminescence, differential thermal and radiochemical analytical techniques are used. The systems under investigation include hydrocarbon and other organic matrices with and without scavengers. The reactions in matrices are studied in the range of 4 K - 200 K.

537. APPLICATION OF COLLISION THEORY TO RELAXATION PHENOMENA AND LASERS \$ 34,200 01-2
R. W. Conn - Department
of Nuclear Engineering

A description of inelastic molecular collisions is fundamental to understanding a host of physical processes, including those affecting the operation of molecular lasers. Unfortunately, these data have frequently been difficult to obtain from experimental or theoretical sources. The aim of this research is to develop and implement new theoretical methods for creating realistic collision problems relevant to molecular lasers. Attention is focused on the HF system, which is of practical importance as an infrared laser. There is fundamental interest in HF with regard to clarifying the role of rotational processes in vibrational relaxation, hence this work should generally aid in understanding the basic nature of vibration-rotation collision phenomena. The decomposition approach and other related unitary methods developed and refined in earlier studies are being utilized in full vibration-rotation scattering calculations performed on the He-HF and Ar-HF collision systems. We have also developed an alternate numerical distorted-wave approach, and its implementation as a practical computational scheme is being explored.

UNIVERSITY OF WISCONSIN (Continued)

538. METAL CATALYZED HYDROGENATION OF CARBON MONOXIDE TO HYDROCARBONS \$ 56,780 02-1
C. P. Casey - Department of Chemistry

The stoichiometric reactions of metal complexes which parallel probable steps in the reduction of carbon monoxide to hydrocarbons are being investigated to determine structural factors which influence the reaction. The synthesis and stability of metal formyl compounds is being investigated to determine the kinetic and the thermodynamic stability of these compounds which have been proposed as important intermediates in the metal catalyzed hydrogenation of CO. Studies of the hydrogenation of metal carbene complexes, studies of the reduction of metal acyl compounds, and studies of the timing of CO insertion into metal carbon bonds are continuing. In addition, studies of the synthesis of bimetallic organometallic complexes for use as possible homogeneous catalysts for the reduction of carbon monoxide are being initiated.

WORCESTER POLYTECHNIC INSTITUTE

539. THE RADIOLYSIS AND PHOTOLYSIS OF HETEROCYCLIC ORGANIC COMPOUNDS \$ 33,288 01-1
A. A. Scala - Chemistry Department

Studies of the gas phase γ -radiolysis and vacuum ultraviolet photolysis of complex organic molecules. The objective is to determine with a greater degree of certainty the primary and secondary modes of decomposition of complex organic molecules and to understand and to codify the factors which affect the reactions in these systems. The concern is with ions as well as neutral excited molecules. Careful study of secondary reactions will permit deduction of information concerning energy distribution in the decomposing molecules. The studies in these systems have led to the proposal of a quasi-equilibrium situation which allows thermodynamic factors such as bond energies to be significant in determining reaction channels. These observations derived from a study of more than twenty molecules have made us confident that areas of absorption, photoelectron and mass spectroscopy, vacuum ultraviolet photochemistry and radiation chemistry can all be correlated to improve the understanding of high energy processes in organic molecules.

WRIGHT STATE UNIVERSITY

540. ATOM AND RADICAL CONCENTRATIONS \$ 45,280 01-2
IN THERMAL REACTIONS OF
HYDROCARBON AND OTHER GASES
G. B. Skinner - Department
of Chemistry

Concentrations of species such as H, O, OH and CH₃ are being determined in shock-heated mixtures of smaller hydrocarbons diluted with argon, sometimes in the presence of oxygen. The method of analysis used is atomic (or molecular) absorption spectroscopy, which has a good combination of high sensitivity and high space and time resolution. These experiments go far toward clarifying our understanding of the high temperature reactions of several hydrocarbons.

YALE UNIVERSITY

541. LIGAND TRANSFORMATIONS \$ 30,000 02-1
AND THEIR ROLE IN METAL
ASSISTED HYDROGENATION
R. D. Adams - Department
of Chemistry

The objective of this research is to develop systems capable of performing the catalyzed homogeneous hydrogenation of isocyanide molecules. The principal goals are to investigate the structural and mechanistic aspects of this reaction. Thus, the work emphasizes the isolation of reaction intermediates, and the study of their patterns of reactivity. The mechanisms of catalytic reactions of CO and H₂ are largely unknown. The similarity of isocyanides and carbon monoxide may result in mechanisms of hydrogenation for both species which are similar. Our procedure is to study the reaction of the combination of hydrogen and isocyanide molecules with specially selected transition metal complexes. The isolation of reaction intermediates and their structural study by x-ray crystallographic methods are being pursued. The reactivity of these intermediates and their exact role in the mechanistic scheme are being explored.

SECTION C
Summary of
Funding Levels

SUMMARY OF
FUNDING LEVELS

During the fiscal year ending September 30, 1978, the Chemical Sciences program total support level amounted to about \$41.3 million in operating funds and \$2.7 million in equipment funds. The equipment funds were expended primarily at DOE Laboratories and Technology Centers and they are not included in the project funding levels shown in this report. The following analysis of expenditures for FY 1978 includes only operating funds.

1. By Region of the Country:

	DOE . Laboratories (%)	Academic Inst. (%)	Total Program (%)
(a) Northeast..... (Conn., D.C., Del., Mass., Md., N.J., N.Y., Pa., R.I.)	22.5	32.2	25.1
(b) South..... (Ala., Fla., Ga., La., Miss., S.C., Tenn., Va., W.Va.)	20.1	9.0	17.3
(c) Midwest..... (Ill., Ind., Iowa, Kans., Mich., Minn., Mo., Nebr., Ohio, Wis.)	34.9	29.6	32.9
(d) West... (Ariz., Calif., Colo., Nev., N.M., Okla., Oreg., Tex., Utah, Wash.)	22.5	29.2	24.7

2. By Institutional Categories:

	Total Program (%)
(a) DOE Laboratories....	76.6
(b) Academic Institutions.....	20.8
(c) Other Government Agencies.....	0.9
(d) Private Sector Corporations.....	1.7

3. By DOE Laboratory

	DOE Laboratories (%)	Total Program (%)
Ames Laboratory.....	6.5	5.0
Argonne National Laboratory.....	20.6	15.7
Bartlesville Energy Technology Center.....	0.4	0.3
Brookhaven National Laboratory.....	22.4	17.1
Lawrence Berkeley Laboratory.....	14.2	10.8
Lawrence Livermore Laboratory.....	0.7	0.6
Los Alamos Scientific Laboratory.....	2.0	1.6
Morgantown Energy Technology Center.....	0.4	0.3
Mound Laboratory.....	2.6	2.0
Notre Dame Radiation Laboratory.....	5.2	4.0
Oak Ridge National Laboratory.....	19.7	15.1
Pacific Northwest Laboratory.....	3.4	2.6
Pittsburgh Energy Technology Center.....	0.1	0.1
Sandia Laboratories - Albuquerque.....	0.2	0.2
Sandia Laboratories - Livermore.....	1.6	1.2

4. By Budget Number/Title

	DOE Laboratories (%)	Academic Inst. (%)	Total Program (%)
01-1 Photochemical and Radiation Sciences.....	25.0	31.4	25.9
01-2 Chemical Physics.....	23.7	17.7	22.4
01-3 Atomic Physics.....	8.8	17.4	10.8
02-1 Chemical Energy.....	21.4	20.4	21.6
02-2 Separations.....	10.8	8.7	10.4
02-3 Analysis.....	9.7	2.4	8.0
02-4 Chemical Engineering Sciences.....	0.6	2.0	0.9

SECTION D

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Index to Budgetary/Programmatic Categories
Index to Energy Research Areas

The indexes refer to the project numbers
in Sections A and B.

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01-1 Photochemical and Radiation Sciences - Photochemistry, with emphasis in areas having potential impact on solar energy concepts such as photosynthesis and photoelectrochemistry; radiation chemistry; hot atom chemistry.

1	28	69	127	136	405	429	457	478	519
2	29	70	128	137	406	430	458	479	520
3	30	71	129	150	407	431	460	482	527
22	54	82	130	151	408	436	463	488	530
23	55	83	131	152	409	441	466	493	531
24	56	89	132	305	410	442	470	494	533
25	57	90	133	306	414	443	471	498	534
26	58	125	134	401	415	455	472	505	536
27	59	126	135	403	424	456	476	518	539

01-2 Chemical Physics - Chemical dynamics, energy transfer, combustion, molecular structure and spectroscopy, theoretical work in quantum chemistry, molecular dynamics and statistical mechanics.

4	34	64	93	110	202	425	452	490	514
5	35	72	94	153	301	426	453	496	515
6	36	73	95	154	308	432	454	501	528
7	60	74	96	155	412	437	467	503	535
31	61	84	97	185	416	444	473	506	537
32	62	91	98	186	418	448	477	508	540
33	63	92	99	187	419	450	486	510	

01-3 Atomic Physics - Molecular, atomic and ion physics: theory and experiments on energy levels, transition probabilities and oscillator strengths; ion-atom collisions; electron and photon scattering, excitation and ionization; x-ray production.

45	50	101	167	184	433	480	495	521	522
46	51	115	168	201	449	481	499		
47	52	116	169	203	459	483	502		
48	80	117	170	309	461	487	509		
49	100	166	171	422	468	489			

02-1 Chemical Energy - Organic, inorganic, physical and electrochemistry; thermochemistry and reaction mechanisms and dynamics; coal and hydrocarbon fuel chemistry, heterogeneous and homogeneous catalysis, chemistry of hydrogen production and storage, biomass conversions.

8	37	76	106	120	161	310	438	492	529
9	38	77	107	143	172	311	439	500	532
10	39	85	108	144	173	413	440	504	538
11	44	86	111	156	174	420	445	507	541
12	53	102	112	157	176	423	451	512	542
13	65	103	113	158	183	427	462	523	
14	66	104	114	159	204	434	469	524	
15	75	105	118	160	307	435	491	525	

02-2 Separations - Isotope effects, isotopic separations, methods of separating and purifying chemical species, separation of substances in different physical states.

16	119	124	148	164	404	446	484	517	526
40	121	145	149	165	411	447	511		
67	122	136	162	302	417	474	513		
78	123	147	163	304	421	475			

02-3 Analysis - Research basic to the enhanced understanding of chemical and physical techniques for analysis of substances important in energy processes.

17	20	42	79	138	141	178	181	402	485
18	21	43	81	139	142	179	182	464	
19	41	68	87	140	177	180	303	465	

02-4 Chemical Engineering Sciences - Fluid dynamics (turbulence), thermodynamics, mass and energy transport, particle dynamics (fluidization), and chemical and physical rate processes. Emphasis is given to improving and/or developing the scientific basis for engineering generalizations, unifying theories and innovative processes.

88	109	175	428	497	516				
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CHEMICAL SCIENCES
ENERGY RESEARCH AREAS

-182-

Atmospheric Chemistry

21	31	45	79	96	177	415	441	471	485
25	42	70	89	150					

Combustion

7	42	74	89	154	301	448	490	514	540
16	55	78	96	175	426	453	503	515	
25	56	84	119	187	437	454	506	528	
31	61	88	150	201	444	486	510		

Fossil Chemistry and Physics

8	37	42	76	119	147	164	176	307	542
14	40	43	85	141	149	172			
26	41	53	118	145	156				

Fusion

26	52	80	146	170	415	480	502	522	530
46	55	101	152	202	449	483	520		
49	62	115	167	203	459	489			
51	78	133	168	309	461	499			

Heterogeneous Catalysis

4	95	102	166	311	439	492	504	524	525
90	96	126	183	412	467	500			
91	97	161	204	438	491				

Homogeneous Catalysis

10	85	144	420	434	462	523	532	538	541
44	107	157	427	435	469				
66	108	174	428	445					

CHEMICAL SCIENCES
ENERGY RESEARCH AREAS

-183-

Hydrogen

12	39	77	111	113	144	158	423	446	497
13	65	78	112	120	146	310			

Isotope Effects and Separations

40	67	122	124	302	417	474	475	484	511
42	78	123	146	404	446				

MHD

31	35	56	184	202	468	495	521		
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Nuclear Fuel Processing

40	121	146	148	163	304	404	421	513	517
78	145	147	162	165					

Resource Recovery

147	162	164	165	304	404	421			
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Solar Photoconversion

3	29	61	72	90	137	406	418	466	534
24	30	66	73	128	151	407	424	488	
27	57	69	82	134	305	408	440	505	
28	59	71	83	136	306	410	458	519	

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