Summaries of FY 1977 Research in the Chemical Sciences

February 1978

U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences
Summaries of FY 1977 Research in the Chemical Sciences

February 1978

U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences
Washington, D. C. 20545
In the Chemical Sciences basic energy research program, scientists at government, university and corporate laboratories conduct research on fundamental interactions, processes and techniques important to the production, use and conservation of energy. The goal is to provide, within the scientific disciplines encompassed by Chemical Sciences, the necessary base of scientific knowledge required to advance the nation's energy technology programs. The research covers a spectrum of scientific and engineering areas and is conducted generally by personnel trained in the disciplines of chemistry, analytical chemistry, chemical engineering, chemical physics, physical chemistry and physics.

The research projects documented in this report were conducted under the aegis of the U.S. Energy Research and Development Administration (ERDA). They constituted the program of the Office of Chemical Sciences in the Division of Basic Energy Sciences.

During FY 1977 a Department of Energy was proposed by the President and enacted by Congress. The new Department of Energy (DOE) came into existence on October 1, 1977. ERDA was incorporated into DOE along with other agencies and elements of the Federal Government. The Chemical Sciences basic energy research program now constitutes the program of the Division of Chemical Sciences in the Office of Basic Energy Sciences (BES) under the Director of the DOE Office of Energy Research.

This program constitutes one element of a wide range of research activity supported by the Office of Basic Energy Sciences. Other basic energy research programs are administered by the BES Divisions of Materials Sciences; Nuclear Sciences; Engineering, Mathematical and Geosciences; and Advanced Energy Projects. The structure of the Office of Basic Energy Sciences is given in the following chart.

This report documents all of the Chemical Sciences basic energy research projects underway during FY 1977 and provides a summary of funding levels and appropriate indexes.

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

The purpose of this report is to provide a convenient compilation and index of the DOE basic energy research program in the Chemical Sciences. This compilation is intended for use by administrators, managers and scientists to help coordinate research and as an aid in selecting new research projects.

The report is divided into Sections A and B describing each of the projects; Section C, a summary and analysis of funding levels; Section D, an index of investigators; and Section E, an index of projects grouped by programmatic area.

Each project carries a number (underlined) for reference purposes. The FY 1977 funding level, title, personnel, budget activity number (e.g. 01-01) and a summary description of the project accompany each project number. 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 1977:

- 01-01 - Radiation Sciences
- 01-02 - Chemical Physics
- 01-03 - Atomic Physics
- 02-01 - Chemical Energy
- 02-02 - Separations
- 02-03 - Analysis
- 02-04 - Engineering Sciences

In the indexes, Sections D and E, the references are to the project numbers appearing in Sections A and B.

It should be recognized that it is impossible to include in this report all the technical data available for such a wide variety and large number of research projects. By the time it could be compiled it would be outdated. The approach taken here was to briefly summarize the actual scope of each project for FY 1977. The best method for obtaining more detailed information about any of the projects is to contact directly the investigators listed.

We wish to express our appreciation to Dr. Jerome Hudis, Brookhaven National Laboratory, and to Dr. Raymond Wymer, Oak Ridge National Laboratory, for their most generous assistance in reviewing, condensing and editing almost all of the original project summary statements, in order that we might achieve the necessary modicum of uniformity in the text of the report.

Thomas W. Buttery
Division of Chemical Sciences
Office of Basic Energy Sciences
# TABLE OF CONTENTS

## SECTION A

<table>
<thead>
<tr>
<th>Laboratories</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ames Laboratory</td>
<td>1</td>
</tr>
<tr>
<td>Argonne National Laboratory</td>
<td>8</td>
</tr>
<tr>
<td>Atomics International</td>
<td>21</td>
</tr>
<tr>
<td>Bartlesville Energy Research Center</td>
<td>22</td>
</tr>
<tr>
<td>Brookhaven National Laboratory</td>
<td>23</td>
</tr>
<tr>
<td>Lawrence Berkeley Laboratory</td>
<td>36</td>
</tr>
<tr>
<td>Lawrence Livermore Laboratory</td>
<td>45</td>
</tr>
<tr>
<td>Los Alamos Scientific Laboratory</td>
<td>46</td>
</tr>
<tr>
<td>Morgantown Energy Research Center</td>
<td>50</td>
</tr>
<tr>
<td>Mound Laboratory</td>
<td>52</td>
</tr>
<tr>
<td>Notre Dame, University of</td>
<td>54</td>
</tr>
<tr>
<td>Oak Ridge National Laboratory</td>
<td>60</td>
</tr>
<tr>
<td>Pacific Northwest Laboratory</td>
<td>72</td>
</tr>
<tr>
<td>Sandia Laboratories (Livermore)</td>
<td>76</td>
</tr>
</tbody>
</table>

## SECTION B

<table>
<thead>
<tr>
<th>Corporations</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerochem Research Laboratories, Inc.</td>
<td>77</td>
</tr>
<tr>
<td>Aerospace Corporation</td>
<td>77</td>
</tr>
<tr>
<td>Bend Research, Inc.</td>
<td>77</td>
</tr>
<tr>
<td>General Electric Company</td>
<td>78</td>
</tr>
<tr>
<td>Stanford Research Institute</td>
<td>79</td>
</tr>
</tbody>
</table>

Other Government Agencies

| National Bureau of Standards/Washington           | 80   |
| National Bureau of Standards/Boulder             | 81   |

Universities

<p>| University of Alabama                             | 82   |
| University of Arizona                             | 82   |
| Baylor University                                 | 82   |
| Boston University                                 | 83   |
| Brandeis University                               | 84   |
| Brown University                                  | 85   |
| University of California/Davis                    | 86   |
| University of California/Irvine                   | 86   |
| University of California/Los Angeles              | 88   |
| University of California/Riverside                | 89   |
| University of California/Santa Barbara            | 89   |</p>
<table>
<thead>
<tr>
<th>University/Institution</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>University of California/Santa Cruz</td>
<td>91</td>
</tr>
<tr>
<td>California Institute of Technology</td>
<td>92</td>
</tr>
<tr>
<td>University of Chicago</td>
<td>93</td>
</tr>
<tr>
<td>Cornell University</td>
<td>94</td>
</tr>
<tr>
<td>University of Delaware</td>
<td>94</td>
</tr>
<tr>
<td>Drexel University</td>
<td>94</td>
</tr>
<tr>
<td>University of Florida</td>
<td>95</td>
</tr>
<tr>
<td>Florida State University</td>
<td>95</td>
</tr>
<tr>
<td>George Washington University</td>
<td>96</td>
</tr>
<tr>
<td>University of Georgia</td>
<td>96</td>
</tr>
<tr>
<td>Harvard University</td>
<td>97</td>
</tr>
<tr>
<td>Howard University</td>
<td>98</td>
</tr>
<tr>
<td>University of Illinois/Chicago Circle</td>
<td>99</td>
</tr>
<tr>
<td>University of Iowa</td>
<td>99</td>
</tr>
<tr>
<td>John Hopkins University</td>
<td>99</td>
</tr>
<tr>
<td>University of Kansas</td>
<td>100</td>
</tr>
<tr>
<td>Kansas State University</td>
<td>100</td>
</tr>
<tr>
<td>Louisiana State University</td>
<td>101</td>
</tr>
<tr>
<td>Marquette University</td>
<td>101</td>
</tr>
<tr>
<td>University of Maryland</td>
<td>102</td>
</tr>
<tr>
<td>University of Massachusetts</td>
<td>102</td>
</tr>
<tr>
<td>Massachusetts Institute of Technology</td>
<td>103</td>
</tr>
<tr>
<td>Michigan State University</td>
<td>104</td>
</tr>
<tr>
<td>University of Minnesota</td>
<td>105</td>
</tr>
<tr>
<td>University of Mississippi</td>
<td>107</td>
</tr>
<tr>
<td>University of Missouri/St. Louis</td>
<td>107</td>
</tr>
<tr>
<td>University of Nebraska/Lincoln</td>
<td>108</td>
</tr>
<tr>
<td>University of Nevada</td>
<td>110</td>
</tr>
<tr>
<td>University of New Mexico</td>
<td>110</td>
</tr>
<tr>
<td>City University of New York/Brooklyn College</td>
<td>110</td>
</tr>
<tr>
<td>State University of New York/Buffalo</td>
<td>111</td>
</tr>
<tr>
<td>Northwestern University</td>
<td>111</td>
</tr>
<tr>
<td>Ohio State University</td>
<td>112</td>
</tr>
<tr>
<td>University of Pennsylvania</td>
<td>113</td>
</tr>
<tr>
<td>Pennsylvania State University</td>
<td>113</td>
</tr>
<tr>
<td>University of Pittsburgh</td>
<td>114</td>
</tr>
<tr>
<td>Princeton University</td>
<td>115</td>
</tr>
<tr>
<td>Purdue University</td>
<td>116</td>
</tr>
<tr>
<td>Rice University</td>
<td>116</td>
</tr>
<tr>
<td>University of Rochester</td>
<td>117</td>
</tr>
<tr>
<td>University of South Carolina</td>
<td>117</td>
</tr>
<tr>
<td>Stanford University</td>
<td>117</td>
</tr>
<tr>
<td>University of Tennessee</td>
<td>118</td>
</tr>
<tr>
<td>University of Texas</td>
<td>118</td>
</tr>
<tr>
<td>Texas A&amp;M University</td>
<td>119</td>
</tr>
<tr>
<td>Texas Southern University</td>
<td>120</td>
</tr>
<tr>
<td>University of Utah</td>
<td>120</td>
</tr>
<tr>
<td>Virginia Polytechnic Institute and State University</td>
<td>121</td>
</tr>
<tr>
<td>Washington University</td>
<td>121</td>
</tr>
<tr>
<td>Wayne State University</td>
<td>122</td>
</tr>
<tr>
<td>College of William and Mary</td>
<td>122</td>
</tr>
</tbody>
</table>
SECTION C

Summary of Funding Levels

SECTION D

Index of Investigators

SECTION E

Index of Projects Grouped by Programmatic Area
SECTION A

LABORATORIES

The information was taken from current Laboratory program budget submissions and project summaries. Most of these projects are of a continuing nature.
Photophysics of organic molecules and solids, mechanisms by which light quanta are converted into heat, chemical energy and different light quanta. The effects of strain, site inhomogeneity and the electron-phonon interaction of vibronic absorption band profiles of molecular solids. Survey of photochemistry and spectroscopy of selected organic compounds, e.g., organosilicon, isotopically selective solid state photochemistry. Solid state photochemical hole burning as a tool for probing the dynamics of photochemical processes as well as the structures of photoreactive states. Specific systems include organosilicon (germanium) compounds and halogen diatomics, e.g., I₂ and ICl. Polariton effects in naphthalene, controlling crystal perfection by chemical doping so that the dynamics of electronic energy transfer can be probed.

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.
3. PICOSECOND SPECTROSCOPY AND PHOTOCHEMISTRY
   W. Struve

   Laser picosecond spectroscopy; systematic design of practical photocatalysts for closed cycles involving water photodecomposition, photochemical H₂ storage and photopolymerization; ultrafast predissociation of gas-phase iodobenzene and ICl; comparisons between the gas-phase and greatly accelerated solution-phase photochemistry of Br₂ and BaO; photodissociation of specific coordination compounds such as \([W(Cp)(CO)_3]_2\) and Co(NH₃)₅I²⁺

4. STATISTICAL MECHANICS OF GASEOUS SYSTEMS
   D. Hoffman

   Interaction of gas molecules with solid surfaces. Identification and characterization of the binding sites for gas atoms or molecules on surfaces. Study of the kinetics of adsorption and desorption processes. Investigation of dissociative adsorption mechanisms. Study of surface distributions established under nonequilibrium conditions. Investigation of the effect of surface coverage on the nature of binding sites. Exploration of interaction between adsorbed surface species. Investigation of surface migration of adsorbates. Study of the effect of surface overlayers on the catalytic properties of surfaces. Kinetic theory of polyatomic gases; transport and relaxation processes; development of reliable collision models from which quantitative calculations of properties of interest can be made; phenomena for which molecular internal structure is of crucial importance such as those involving inelastic collision mechanisms.

5. MASS SPECTROSCOPY, ION SOURCE CHEMISTRY
   H. Svec

   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.
AMES LABORATORY
Molecular Sciences -01- (Continued)

6. MOLECULAR BONDING THEORY
   K. Ruedenberg
   $185,000 01-02

Quantum mechanical ab initio methods for useful descriptions of reactive molecular changes by means of simple but effective procedures; quantitative insights into the occurring electronic rearrangements and quantitative implications for reaction energetics and kinetics. Reactions involving a variety of small and medium sized molecules.

7. ATOMIC, MOLECULAR, AND FREE RADICAL CROSSED BEAM KINETICS
   C. Ng
   $10,000 01-02

Reactions of hydrocarbons with oxygen; combustion reactions; free radical chain reactions; stable combustion products; molecular beam photoionization mass spectrometry; crossed molecular (or atomic) beam techniques.
CHEMICAL KINETICS AND REACTIVITY OF TRANSITION METAL COMPLEXES
J. Espenson

Transition metal complexes in reactions pertinent to coal use and conversion. Kinetics of rate-limiting molecular processes through model compounds and idealized reactions. Metal-carbon bonds and alkyl transfer reactions. Results contribute to design of syntheses of new hydrocarbon derivatives of transition metals for further study.

PROPERTIES OF RARE EARTH ELECTROLYTES
F. Spedding

Basic study of aqueous solutions of electrolytes taking advantage of the special aspect of the rare earth cations as predominately changing 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.

METALLIC AND INORGANIC HYDRIDES WITH POTENTIAL APPLICATION IN HYDROGEN STORAGE
J. Espenson

Structural and electronic properties for high hydrogen affinity and capacity. Chemistry-physics-metallurgy of metal-hydrogen interactions for hydrogen storage. LaNi₅ 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 H₂ 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.
11. THERMOCHEMICAL CYCLES $95,000 02-01
FOR THE PRODUCTION OF
HYDROGEN FROM WATER
D. Martin, D. Ulrichson

Investigation of chemical materials and cyclic reaction systems for the
decomposition of water into hydrogen and oxygen; phase characterization,
thermodynamic properties, and kinetic behavior at temperatures up to
1000°K; lab-scale experiments with certain rare earths, and utilizing
reaction steps common to several thermochemical cycles, e.g. oxygen
generation by chlorine; engineering techniques to provide economic factors,
optimization, comparative evaluation and equipment scaleup of different
cycles.

12. MULTIPLE PULSE NMR $35,000 02-01
STUDY OF THE CHEMICAL
CONSTITUTION OF COAL
B. Gerstein

Correlation of chemistry with solid-state electronic and molecular
properties, specifically for coal chemistry. Aliphatic/aromatic ratios
(and average ring sizes) in coal by high resolution proton spectra, using
newly developed combined multiple pulse - magic angle spinning technique
for narrowing dipolar-broadened spectra of carbon and hydrogen. Combined
cross polarization - magic angle spinning technique being developed for
\(^{13}\)C nuclei in coals.

13. DIFFRACTION STUDY OF $35,000 02-01
COAL STRUCTURES
J. Clardy

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).
14. SEPARATIONS RESEARCH

J. Powell

Cation-exchange and extractive systems to produce pure (natural) lanthanides and to partition actinides and lanthanides for management of nuclear wastes. Synthesis of new chelatants and chelates. Study of stabilities, separation factors, synergism; isolation of lanthanides and actinides. Introduction of organophilic-hydrophobic substituents into chelates.

15. ANALYTICAL SPECTROSCOPY

V. Fassel

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

16. ANALYTICAL SEPARATIONS

J. Fritz

New chemical analyses and separations, particularly chromatographic, for direct use and for analytical support of other research. Organics; simplified analyses of trace organics in water, related to fossil fuels. Development of highly selective chelating resins for metal ions.

17. ANALYTICAL MASS SPECTROSCOPY

H. Svec

Contamination-free trace impurity analyses by mass spectrometry with minimal sample manipulation. Spark source with isotope dilution for solids; focused laser - d.c. arc ion source for small regions or bulk samples; hollow-cathode discharge ion source for analyzing untreated (frozen) aqueous solutions. Gas chromatography-mass spectrometry-extraction for organic impurities in water and gases.
18. ACTIVATION ANALYSIS $59,000 02-03
   A. Voigt

Application of neutron activation and neutron capture gamma ray analysis to energy and health problems. Trace element characterization of coals, interrelation of coal deposits; potential on-line plant analysis for S, Fe, moisture. Trace elements in blood, correlation with pathologies, removal of interferences due to Na and Br.

19. LASERS IN ANALYTICAL CHEMISTRY $96,000 02-03
   E. Yeung

Identification and demonstration of improved analytical sensitivity and reliability through use of lasers and modern optics. Development of Fabry-Perot detection (atomic emission from spark sources) and laser-excited atomic fluorescence (flame and non-flame sources) for improved sensitivity in element detection; finding paths of trace elements from fossil fuels; Raman and Stokes-Raman scattering for combustion studies; time-synchronous Raman scattering for remote monitoring of combustion chambers.

20. ATMOSPHERIC POLLUTION MONITORING BY DIODE LASERS $96,000 02-03
    E. Yeung

Determination of reliable spectral line widths and positions for atmospheric components in order to realize the potential high resolution for pollutants available with infrared diode lasers. Experimental comparisons (diode lasers vs conventional IR spectrometers) plus theoretical models to provide dependable line information. Evaluation of monitoring at an actual source. Spectral interferences identified and perhaps eliminated; long-path measurements; remote sampling.
The program includes: chemical reactions of e\text{aq} and OH radicals and their precursors on the picosecond time scale; chemical consequences of inhomogeneous deposition of ionizing radiation (e\text{aq} completed, OH being studied); solvation of the electron in various solvents; magnetic field effects on ion recombination; radical-radical interactions studied by NMR and ultrafast EPR spectroscopy; activation energies for reactions between radiolytic products in solution; pulse radiolysis using high LET ions. Linac accelerator with associated optical detection methods extending down into the 50 picosecond range, streak camera technique, ultrafast EPR and fast-flow NMR methods. The fast pulse radiolysis program studies energy deposition processes that result from the absorption of radiation, the kinetics of the very fast chemical processes initiated by radiation, and the temperature dependence of reactions occurring among the radiolytic products of water.

Phenomenon of electron tunneling and the mechanisms of energy transfer and radical reactions in the gas phase; electron transfer between molecules separated by 10-40 Å of inert solvent; effect of molecular structure and thermal energy on the rates of intermolecular electron transfer. Study of electron tunneling reactions as mechanisms for molecular rectification essential to the separation of positive and negative charge in photosynthesis and possible utility in man-made solar energy conversion devices. Energy absorption and transfer in irradiated gas mixtures; light emission from excited states used to probe the kinetics and mechanisms of processes occurring; choice of possible mechanisms of excited state formation (i.e., direct excitation, intramolecular relaxation processes, energy transfer, and ion recombination) on the basis of time-resolved fluorescence measurements; rare gases and rare gas-iodine mixtures.
ARGONNE NATIONAL LABORATORY
Chemistry Division -01- (Continued)

23. PHOTOCHEMISTRY IN AQUEOUS SOLUTION AND CHEMICAL STORAGE OF SOLAR ENERGY
   M. S. Matheson

Solutions containing solutes such as ferricyanide, which upon photolysis produce hydrated electrons are studied to optimize \( \text{eq.} \) production with longer wavelength light as a means for \( \text{H}_2 \) production. Investigation of systems in which sunlight stimulates oxidation-reduction reactions in pairs of solutes wherein some of the products can be kept from recombining, thus storing energy; \( \text{MnSO}_4-\text{ZnSO}_4 \) system with storage products being \( \text{H}_2 \) and \( \text{MnO}_2 \).

24. RESEARCH IN COMBUSTIBLE FUELS
   S. Gordon

Research in free radical processes applied to reactions with coal model compounds, hydrogen production by direct reaction of carbon with water, and hydrogen production from water utilizing ultraviolet light; elimination of organically bound sulfur. Pulse radiolysis of coal model compounds in a variety of liquids to study kinetics and to observe intermediates; final products for identification obtained by steady gamma radiolysis; reactions of \( \text{OH}, \text{O}^\cdot, \text{H} \) and solvated electrons with various thiopenes.

25. COMBUSTION, ATMOSPHERIC AND ENVIRONMENTAL CHEMISTRY
   S. Gordon, L. Kaplan

Pulse radiolysis techniques to study reactions involving radical species \( \text{OH}, \text{HO}_2 \) and \( \text{Cl} \) with compounds (organic and inorganic) introduced into the atmosphere by the combustion of fossil fuels and by the widespread use of pesticides and aerosol propellants. Development of a condensation nucleus size analyzer capable of determining the size and number of particles from 5 to 500 Å in size; study of the chemistry and physics of aerosols generated from various atmospheric pollutants.
26. SPECTROSCOPIC AND THEORETICAL STUDIES ON CHLOROPHYLL, PHOTOSYNTHESIS, AND ENERGY TRANSFER
   J. J. Katz

Laboratory studies on chlorophyll by nuclear magnetic resonance spectroscopy; nature of intermolecular chlorophyll interactions; $^1\text{H}_{\text{mr}}$, $^{13}\text{C}_{\text{mr}}$ and $^{15}\text{N}_{\text{mr}}$ spectroscopy to delineate the role of the central magnesium atom in chlorophyll and the general nature of chlorophyll-chlorophyll and chlorophyll-ligand interactions. New methods developed to record nmr spectra under light irradiation to determine chlorophyll triplet hyperfine coupling constants. $^{13}\text{C}_{\text{mr}}$ studies on chlorophyll incorporated into lipid vesicles and photosynthetic membranes to ascertain the state of the chlorophyll in these systems. Optical studies on ordered monolayer arrays of chlorophyll to deduce the spectral consequences of particular geometries; photoelectron spectroscopy to establish the energy of binding of valence and structural electrons in chlorophyll aggregates; chlorophyll lasers to investigate the origins and significance of fluorescence in photosynthesis and excited chlorophyll states generally. Ab initio calculations, exciton, and Förster transfer theory to study excited state properties, light absorption, and energy transfer properties of chlorophyll.

27. STUDY OF PHOTOSYNTHESIS
   WITH ESR AND ENDOR
   J. R. Norris

Time-resolved esr spectroscopic studies of photosynthesis; development of spin echo esr spectrometer with ten nanosecond time resolution to permit direct observation by esr of primary energy production steps in photosynthesis. Goals are to determine the distance of electron transfer, identification of necessary transient stages in photochemistry, and determination of whether photochemistry proceeds from the singlet or triplet state. Esr used to measure energy degraded to heat during photosynthesis; newly developed endor procedures used to measure coupling constants of doublet and triplet chlorophyll states important in photosynthesis.
28. SOLAR ENERGY CONVERSION

J. J. Katz

Development of devices which mimic the photosynthetic apparatus of plants and photosynthetic bacteria; artificial photosynthesis systems that successfully mediate electron transfer between electron donors and acceptors; successful generation of voltages as high as 400 mV. Use of artificial-linked photoreactive chlorophyll dimers as the working elements in the "synthetic leaf"; attachment of an antenna to the synthetic reaction centers to duplicate the photosynthetic light conversion apparatus of a green plant. Electrochemical studies on chlorophyll; interaction of charged chlorophyll species with electron donors and acceptors; energetics of chlorophyll excited states produced electrochemically; oxidation-reduction properties of in vivo and synthetic reaction centers.

29. PREPARATION OF BIOLOGICAL MATERIALS OF UNUSUAL ISOTOPIC COMPOSITION AND ASSOCIATED NEUTRON AND X-RAY STRUCTURAL STUDIES

J. J. Katz

Large-scale culturing of unusual isotopic composition; organisms highly enriched in deuterium, carbon 13, and nitrogen 15; chlorophylls, chlorophyll-protein complexes, electron-transfer proteins, chloroplasts, and chromatophores. Development of new methods for isolating chlorophyll-protein complexes and photoreaction centers, using fluorinated surfactants and other exotic surface-active agents. Procedures for disaggregating and then reaggregating photosynthetic membranes with deuterated or \(^{13}\)C-chlorophyll and a lipid matrix of ordinary isotopic composition for nmr and small-angle neutron scattering studies. Preparation of the halophilic bacterium Halobacterium halobium (an organism that carries out photosynthesis using the pigment bacteriorhodopsin instead of chlorophyll) in fully deuterated form, for the study of bacteriorhodopsin and the light-utilizing apparatus of this organism by small-angle neutron scattering, nmr, and resonance enhanced Raman spectroscopy.
30. HIGH RESOLUTION SPECTROSCOPY $218,000 01-02
H. M. Crosswhite

Examination near the ionization threshold of energy levels of atomic uranium, plutonium and several lighter elements such as Ba, including transition probability determinations (hook method) and quadratic Zeeman effects. Relations between energy level positions and transition rates analyzed by the multichannel quantum defect theory. Theoretical analysis of empirical energy levels of U, Np, Pu and Es atomic and singly-ionized spectra, emphasis on configuration-mixing modeling relating to isotope-shift analysis and development of a systematic model for prediction of the electronic and thermodynamic properties of heavy and superheavy materials and plasmas. Experimental and theoretical studies of actinide ions (U through Es) in crystals; development of a model of 5f electronic energies for use in atomic and solid-state energy level calculations. Fundamental problems of simple diatomic molecular systems such as $\text{H}_2$, $\text{D}_2$, $\text{T}_2$, OH, OT, $\text{N}_2$ and $\text{N}_2^+$ relating to verification of ab initio calculation methods and energy-transfer phenomena in atmospheric species.

31. CROSSED-BEAM STUDIES OF $193,000 01-02
REACTIONS OF ACCELERATED
ATOMS AND MOLECULES
S. Wexler

Dynamics and energetics of chemi-ionization and other (usually) endoergic reactions. Accelerated crossed-molecular beams; ionic (and sometimes neutral) collision products analyzed in flight in two "chemical accelerator" machines; chemi-ionization and other hyperthermal processes. Reactions investigated are associative ionization, rearrangement (reactive) ionization, electron transfer, collision-induced ion pair formation (polar dissociation), and inelastic scattering. Energy transfer in collision processes.

32. THEORETICAL CHEMISTRY $286,000 01-02
AND MODELING
A. C. Wahl

Chemical dynamics theories developed and applied both to efforts in chemi-ionization and isotope separation, and to evaluate the reliability of current methods of calculating potential energy curves and surfaces. The fundamental properties of atmospheric molecules calculated on a consistent basis to provide molecular characteristics as input to aeronomic modeling. New methods of calculating the fundamental properties of molecules, particular emphasis on heavy atom systems. Computer code development; a library of computer codes in molecular quantum mechanics, scattering theory, and graphics display. Function of chlorophyll in photosynthesis at the molecular level by a variety of computational techniques.
33. MOLECULAR SPECTROSCOPY $133,000 01-02

J. Ferraro

Molecular spectroscopy, changes in properties using optical probes, such as electronic, infrared, and Raman spectroscopy; absorption spectra at ambient and non-ambient conditions of temperature and pressure, using dispersive infrared instrumentation as well as interferometric and Fourier-transform spectroscopic techniques. Theoretical calculations (normal coordinate analysis) on molecules for structural verification. Materials being investigated include: one-dimensional conductors (e.g., K$_2$[Pt(CN)$_4$]Br$_{0.3}$3H$_2$O, K$_{1.75}$[Pt(CN)$_4$]·1.5H$_2$O), ionic conductors (e.g., Cu$_2$HgI$_4$, Ag$_2$HgI$_4$), semiconductors (e.g., alkaline-earth, rare-earth monochalcogenides), superconductors (e.g., A$_3$B alloys), thermochromic materials (e.g., Cu$^{2+}$, Ni$^{2+}$ coordination compounds). Synthesis of new superconducting phases.
34. PHOTOIONIZATION AND PHOTO-
ELECTRON RESEARCH
  J. Berkowitz, J. H. D. Eland

Studies of basic interactions of atoms and molecules by photoionization and
photoelectron spectrometry techniques: CO$_2^+$, heat of formation of S$_2$O, heat
of formation and structure of C$_4$H$_8$, decay modes for excited species, photo-
ionization of N$_2$O, HI, DI, and Xe, photoionization of water and ammonia,
photoelectron spectroscopy of ZrCl$_4$ and C$_2$Cl$_6$. Theoretical studies of:
electron-atom and ion high-energy inelastic collisions, hydrogenic coherence
effects, dissociation processes of polyatomic molecules, and high-energy
ion-atom collisions.

35. INTERACTIONS OF ENERGETIC
PARTICLES AND PHOTONS
WITH SOLIDS
  M. Kaminsky

Atomic and molecular phenomena that occur during the interaction of energetic
particles (0.5 keV - 100 keV range) and photons (keV range) with the surfaces
of solids. Identification of the important processes which contribute to
the release of atomic and molecular species in different charged states
from surfaces under light-ion bombardment in the 0.5 keV - 100 keV range:
particle release dependence on the dose of the trapped incident ions, and
on the stored energy in near surface regions. Fundamental studies of
the mechanism leading to the release of atomic and molecular species from
surfaces under energetic (keV) photon impact: photodesorption studies of the
types and amounts of gases released from surfaces under x-ray impact
(mean photon energy 18-24 keV), H$_2$, H$_2$O, O$_2^-$, CO$_2$; mean desorption yields
as a function of mean photon energy.

36. LASER AND RF SPECTROSCOPY
OF FREE ATOMS AND MOLECULES
  L. S. Goodman, W. C. Childs

Laser and radiofrequency techniques used for high-resolution studies of the
structure of molecules and free atoms: hyperfine structure and isotope
shifts in heavy atoms, vapor phase actinide molecules, spectroscopy of the
positronium atom.
ARGONNE NATIONAL LABORATORY
Physics Division  -01- (Continued)

37. MOSSBAUER EFFECT PROGRAM
G. Perlow

$175,000   01-03

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.

38. BEAM-FOIL RESEARCH AND COLLISION DYNAMICS OF HEAVY IONS
H. G. Berry

$265,000   01-03

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).

39. DISSOCIATION AND INTERACTION OF ENERGETIC MOLECULAR ION BEAMS IN SOLID AND GASEOUS TARGETS
D. S. Gemmell

$175,000   01-03

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° and $\sim$250 eV) for the breakup fragments arising when such beams bombard thin (~100 Å) foils. Interaction between the projectiles and the polarization oscillations induced in the target foil. Transmission of molecular ions through foils, properties of incident molecular ions and their effective charges inside matter.
The inorganic chemistry program continues its strong emphasis on fluorine chemistry and on studies of the basic chemistry and applications of unusual oxidizing and fluorinating agents, such as the compounds of the noble gases. Strong support is being given to the solution of chemical problems arising from the chemi-ionization process for uranium isotope separation now under development. Methods for maintaining UF$_5$ in solution have been discovered, a fact that may be useful for the separation of uranium isotopes by chemical exchange with UF$_6$ in the gas phase. This possibility will be investigated further. Work continues on development of solid absorbers for the chemical trapping of radon, xenon, and, perhaps, krypton.

Investigation of logical diagenesis: biological materials - peat - lignite - sub-bituminous - bituminous - anthracite. Correlation with chemical structures of petroleums, 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 chromatography and fractional distillation.
Thermochemical cycle of chemical reactions using heat to dissociate water into hydrogen and oxygen, a "chemical heat engine." The cycle under study at Argonne, designated ANL-4, is:

$$2\text{NH}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O} + 2\text{KI} \xrightarrow{\text{ambient temp.}} 2\text{KHCO}_3 \xrightarrow{\text{in solution}} 2\text{NH}_4\text{I} ;$$

$$2\text{KHCO}_3 \xrightarrow{425 \text{ K}} \text{K}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 ;$$

$$\text{Hg} + 2\text{NH}_4\text{I} \xrightarrow{700 \text{ K}} \text{HgI}_2 + 2\text{NH}_3 + \text{H}_2 ;$$

$$\text{HgI}_2 + \text{K}_2\text{CO}_3 \xrightarrow{1000 \text{ K}} \text{Hg} + 2\text{KI} + \text{CO}_2 + \frac{1}{2} \text{O}_2$$

These reactions split one mole of water and proceed as written without serious side reactions. The maximum temperature, 1000°K, may be supplied by a high-temperature gas-cooled nuclear reactor. After completing a plausible preliminary flow diagram, efforts are directed toward specific information about the cycle that will permit a detailed engineering analysis of its operation.

In addition, fundamental research is included in related areas, such as the behavior of ammonium halides and alkali carbonates in various solvent systems and the high-temperature chemistry of the ammonium halides.
ARGONNE NATIONAL LABORATORY  
Chemistry Division -02- (Continued)

43. CHEMICAL SEPARATIONS SCIENCE  
   E. P. Horowitz  
   $500,000  
   02-02

Liquid-liquid extraction, liquid and bonded-phase chromatography, interfacial 
mass transfer, adsorptive bubble separation, exclusion chromatography, and 
field flow fractionation. Synthesis, purification, and testing of reagents. 
Identification and evaluation of the system variables to elucidate 
Applications to separation of actinides and the fission products $^{99}$Tc and 
$^{129}$I from nuclear wastes, separation of polymers and colloids (Pu polymer, 
nonextractable Zr), kerogen and bitumen from shale oil, coal constituents.

44. ANALYTICAL DEVELOPMENTS  
   IN MASS SPECTROMETRY-  
   CHROMATOGRAPHY AND 
   SUPPORTING SYSTEMS  
   M. H. Studier  
   $135,000  
   02-03

Improvement of instruments, procedures, and data handling systems for 
support of programs in (particularly) fossil energy. Time-of-flight mass 
spectrometers in combination with chromatographic and high vacuum techniques 
of separations. Aromaticity of fossil fuels by fluorination.

45. STUDY OF ATMOSPHERIC  
   TRACE GASES BY MASS  
   SPECTROMETRY  
   C. M. Stevens, E. H. Appelman  
   $110,000  
   02-03

Isotopic composition of atmospheric CO to determine its principal source. 
Mass spectrometric measurement of $^{14}$C in atmospheric CO to determine the 
ratio of dead carbon to live carbon sources. Laboratory measurements of 
isotope fractionation in OH oxidation of CH$_4$ + CO and CO + CO$_2$ to aid in 
analysis of data on samples of atmospheric CO. Isotopic composition in 
southern hemisphere to explain lower level. Analysis for tropospheric 
and stratospheric concentrations of OH and HO$_2$ important in validating 
photochemical models of effects of trace gas pollutants. The analysis 
involves tagged reactants and mass spectrometry.
Development of nuclear analytical techniques for biological systems.
Investigation of mechanism of sulfur uptake into peat, pertinent also to lignite and coal; possibly useful in sulfur elimination from coal.
Previous development completed on preparation of immunologically competent $^{211}\text{At}$-tagged antigens.
Critical test of reaction catalysis in a fluid stream by a suspension of immiscible liquid droplets; reversible reaction to transfer homogeneous catalyst from a carrier phase to a working phase (partition catalysis); formation of surface-active catalyst at interfacial film between the carrier and working phases (surfactant catalysis); emphasis on hydrogenation of aromatic molecules and valence isomerization of highly-strained molecules; comparison of homogeneous and two-phase systems using understood test reaction.
Investigation of reactions in molten sodium carbonate; different catalytic effects of sulfide and sulfate compounds in sodium carbonate on the air or CO₂ oxidation of reactive carbon and of carbon in coal; reactions between typical coal ash components (alumina, iron oxides, iron sulfide, silicon dioxide) and molten sodium carbonate; reactions of calcium oxide and sodium silicates with molten sodium carbonate.
Determination of thermodynamic property data for condensed-ring aromatic and hydrosubstituted compounds present in syncrudes from coal, shale oil, and heavy petroleum ends; preparation of broad-range correlative equations based on chemical structure; basic data measurements include enthalpy of combustion, low-temperature calorimetry, vapor-flow heat capacity calorimetry, PVT relations, vapor pressures, and Raman and infrared spectroscopy.
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; superoxide radicals in biological systems; infrared spectra of protonated molecular clusters in gas phase; reactive metal ion intermediates in redox reactions.

Chemistry of energy-rich atomic and molecular species studied 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 provide 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. Applications include: relation of spin state of carbon-11 atoms and their chemical reactivity; facile reaction rate determinations of atomic species such as carbon, silicon, and the halogens with a broad spectrum of substrates; and a variety of techniques for labeling compounds of medical and biological interest.
Effects on chemical reaction rates by the distribution of reactant energy among translational, rotational, vibrational, and electronic degrees of freedom; energy distribution in the products as a probe of the reaction mechanism; collisional transfer of energy from excited atoms or molecules. Reactions where the well-defined electronic energy of a photoexcited atom or molecule can be transferred to a ground-state atom or molecule, or the excited species can spontaneously lose energy by emission of fluorescence radiation at a rate determined by the natural lifetime of the excited species; competition between energy transfer and emission; fluorescence lifetime; bimolecular rate constant for energy transfer. Direct measurements of lifetimes in the range 1-100 nsec by the single-photon time correlation method.

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 excited states through studies of their reactions with inorganic oxidants and reductants in solution and through their electrochemical behavior at wide band-gap semiconductors. 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 chemical back reactions of transition metal complexes.
54. SELECTIVE LASER-INDUCED CHEMISTRY
D. Brenner

A new program in 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.

55. PICOSECOND SPECTROSCOPY
T. Netzel

Exploration of sub-nanosecond photochemical processes; picosecond absorption spectroscopy; development of picosecond Raman spectrometric methods; modeling of electron photoejection; excited state geometries and reactions.

56. NEUTRON AND X-RAY STUDIES OF MOLECULAR STRUCTURE AND DYNAMICS
H. Bernstein, T. Koetzle, R. McMullan, R. Thomas

Methods of x-ray and neutron diffraction combined with computing and computer graphic techniques to solve significant problems in molecular structure. Emphasis on crystal structures where hydrogen atoms are important and on disordered or partially-ordered structures, since this is where neutron diffraction, alone or in combination with x-ray diffraction, has unique advantages for determining molecular structure and investigating chemical bonding. Systems being investigated are transition metal hydride coordination complexes, hydrates, ferroelectrics, and organic crystals. Combined x-ray and neutron diffraction (X-N) methods to examine the molecular charge-density distributions associated with formation of hydrogen bonds. Improved techniques for on-line network access to structural data bases, and use of interactive computer graphics to evaluate crystallographic results.
Theoretical elucidation of mechanisms of energy flow in chemical reactions; theoretical models for the role of molecular interactions in the storage and interconversion of energy, both in the gas phase and in condensed phases; phenomena associated with charged spheres, such as solvation and charge-transfer processes. Development and implementation of techniques for \textit{ab initio} and semiempirical calculation of the energetics and equilibrium nuclear geometry (structure) of a variety of chemical systems in specific electronic states; classical and semiclassical treatments of the nuclear motion in kinetic processes involving these systems; aqueous electron transfer reactions, hydrogen bonding in hydroxylic systems, \textit{ab initio} models for nickel surfaces, dielectric effects of solvents surrounding cavities of various shapes, dynamics and energetics of hydrogen combustion reactions and the development of a unified semiclassical theory of non-adiabatic transitions in molecular collisions.

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 adsorption 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 of the kinds that may be required for heating and compression of thermonuclear reaction fuel elements.
Crossed molecular beam technique in which one of the reagent beams is labeled with short-lived ($\lesssim 10^{-1}$ 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 HAt + Cl,Br $\rightarrow$ At $+$ 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 $10^{-5}$ A$^2$ can be subjected to differential study. Experimental determinations of reactive potential hypersurfaces to test and calibrate semiempirical theories now under development.

Neutron scattering measurements to obtain structural and dynamic properties of solids. Magnetic systems; spatial distribution of magnetization, its response to applied fields, and behavior of spontaneous magnetic fluctuations; complete characterization of the magnetic ordered and disordered states as well as the interesting critical region in the neighborhood of the ordering transition. Arrangement of atoms and dynamics of motion of nonmagnetic solids.
INVESTIGATIONS OF THE CHEMISTRY OF ENERGETIC COMPOUNDS

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.

KINETICS AND MECHANISMS OF CHEMICAL PROCESSES RELATED TO THE DEVELOPMENT AND USE OF ENERGY

J. W. Sutherland

Basic kinetic and mechanistic details in specific chemical systems associated with the development and use of energy sources 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 sulfur dioxide in the gas phase and in aqueous solution and chemistry of transient intermediate nitrogen-hydrogen compounds.

PORPHYRIN CHEMISTRY

J. Fajer

Synthetic, structural, theoretical and physical chemistry of porphyrins; electronic structure and chemical properties of porphyrins and their radicals; biological role of porphyrin ions in photosynthetic and metabolic reactions; applications of these catalytic reactions to energy conversion systems such as solar energy production of electricity by photo-excitation of porphyrins deposited on solid interfaces or isolated in micelles, the production of hydrogen and/or oxygen in solution using porphyrins to mimic the photosynthetic cell and photo-decompose water, and also to fix nitrogen photochemically via porphyrin derivatives. Techniques include optical absorption, electron spin resonance (esr), nuclear magnetic resonance (nmr) and electron nuclear double resonance (endor). Redox reactions induced chemically, photochemically and electrochemically.
64. BIOELECTROCHEMISTRY AND ELECTROCHEMISTRY
   $109,000 01-02
   S. Feldberg

   Ion location and translocation in bilayer lipid membranes (BLM's); theory as well as several novel experimental techniques (charge pulse and inner voltage clamping) for determining the position of ions absorbed with a BLM. Electron transfer through and/or within BLM's; kinetics and mechanisms of electron transfer between excited states of molecules (porphyrins or ruthenium complexes) within the BLM and electron acceptors or donor located either within the BLM or in the aqueous phase. Computer-simulation and analysis of the behavior of photoelectrochemical transducers to test both the validity of the theory as well as the performance of the device.

65. MOLECULAR STRUCTURE OF PORPHYRINS AND PHOTOENERGY TRANSDUCING SYSTEMS
   $62,000 01-02
   L. Spaulding

   X-ray diffraction techniques in conjunction with other structural probes to determine the molecular and crystal structures of porphyrins, chlorins, and other energy transducing systems; compounds that are models of the natural solar energy conversion systems to fully interpret electron spin resonance (ESR), nuclear magnetic resonance, Raman spectroscopy, and theoretical calculations of these systems.

66. COMBUSTION STUDIES ON ALTERNATE FUELS
   $206,000 01-02
   R. Klemm

   Investigation of unconventional or alternate fuels that may be used to supplement or replace petroleum derived fuels for operation in internal combustion engines and stationary combustion devices; study of the combustion and pollutant formation processes that occur during the use of these fuels. Single cylinder test engine (ASTM-CFR engine) and flat-flame burners used to provide realistic test bases for measuring the effects of operating parameters, such as fuel type and air-fuel ratio, on the pressure, temperature and concentration profiles for stable and transient species that exist during the combustion of various fuels; potential importance of specific elementary chemical reactions that occur during the combustion process. Specific modes and rates of the indicated chemical reactions determined in controlled and isolated experiments that eliminate the complexities of actual combustion devices; combustion modeling studies.
Properties of highly ionized species found as fusion plasma contaminants; mechanisms for production of inner-shell vacancies in heavy ion-atom collisions; measurements of the impact parameter dependence and total cross sections for production of characteristic x-rays; beam foil spectroscopy measurements in the x-ray and vacuum ultraviolet regions to determine lifetimes and investigate atomic structures; cross sections for electron impact excitation and ionization of highly ionized heavy ion beams for the electron energy range up to 20 keV. Three-stage MP Tandem Van de Graaff, beams of ions ranging from H to U with energies up to 250 MeV; 3.5 MV Van de Graaff for low energy, light ions.
68. ENZYME AND ORGANIC MECHANISMS AND ENERGY STORAGE IN ENZYME SYSTEMS
   S. Seltzer

Mechanisms of photosensitized and enzymically and chemically catalyzed cis-trans isomerization and how they can be utilized to maximize the energy difference between photostationary and thermodynamic equilibrium states; synthetic photogalvanic cell from photoisomerization of fumaric to maleic acid.

69. STRUCTURE AND BONDING IN METAL-HYDROGEN SYSTEMS
   J. Hudis, M. L. Perlman

Photoelectron spectroscopy and diffraction methods applied to metal hydrides and their parent metals and alloys; data combined when possible with magnetic, Mössbauer, or other information and analyzed by use of theory in terms of the configurations in valence and conduction band levels of the materials. Practical methods of storing hydrogen as hydrides.

70. LASER-INDUCED REACTIONS FOR ISOTOPE SEPARATION
    R. Weston

Application of laser photochemistry to isotopic enrichment of lighter elements such as C, N, O, or S; unimolecular reactions, bimolecular reactions, and photodissociation processes of vibrationally excited molecules; selective removal of photo-excited molecules. Details of the laser energy absorption process and energy transfer from excited species to provide basic information needed to estimate the efficiency of the isotope separation method.
Extension and improvement of nuclear methods of elemental analysis for many components including trace impurities quickly and efficiently; develop methods of computer-based multivariate statistical analysis for analysis of large amounts of data. Determination of 38 chemical elements in pine needles from living trees, and relation to air pollution; correlation of trace impurity patterns with geographic origin in metals, clays, and other minerals and in man-made artifacts fabricated from these materials. Improved dating techniques with thermoluminescence, lead-210 and carbon-14; thermoluminescence as an indicator of geographic origins and as a mineral resources prospecting method; lead-210 methods to study its uptake from the atmosphere and to differentiate between its introduction into the atmosphere, either naturally or artificially; carbon-14 dating for analysis of relatively small samples. The sub-surface structures and chemical compositions of objects, such as oil paintings by means of neutron activation autoradiography.
72. METAL HYDRIDES
R. 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.

73. HIGH TEMPERATURE CHEMISTRY
J. J. Egan

Investigation of thermodynamic and transport properties of substances at high temperatures; atomic models; development of techniques of solid state electrochemistry; movement of electrons and electron holes in ionic crystals and molten salts; substances include solid and liquid state semiconductor alloys; application to solar cells, high energy batteries, solid and molten salt electrolytes, fuel cells, and high temperature reactor fuels.

74. CHEMISTRY AND PHYSICS OF COAL UTILIZATION
D. R. Mackenzie, R. T. Yang

Mechanisms of hydrogen reactions with coal including the kinetics of pyrolysis and hydrogen reactions in the competition between depolymerization (desired) and char formation in solvent refined coal (SRC) processes.

75. CYCLIC SEPARATIONS
F. B. Hill

Application of cyclic processes to separations of interest in nuclear reactor technology; heatless fractionation, parametric pumping, cycling zone adsorption, and preparative chromatography; experimental investigations of protium-tritium separation by heatless fractionation using the hydrogen-vanadium hydride system; equilibrium and kinetic measurements; theoretical model to predict process performance. Process design studies; measurement of fluid-solid separation systems.
76. DETERMINING FRAGILE MOLECULES IN THE ENVIRONMENT

L. Newman, R. Tanner

Derivatization-chromatography-specific element detection for new high-sensitivity and -selectivity analyses for environmental traces of reactive substances; molecular stability obtained by derivatization. Element specific detectors for greatly increased sensitivity. Potentially applicable to dynamically varying concentrations of (aqueous) phosphate, nitrate, nitrite, (atmospheric) ammonia, nitric acid, particulate sulfates in the environment.
77. DEVELOPMENT AND APPLICATIONS $105,000 02-03
OF NUCLEAR PARTICLE MICROSCOPY
K. W. Jones, H. W. Kraner

New techniques for quantitative measurement and precise spatial localization of stable isotopes; demonstration of applications in fields such as biology, medicine, marine science, solid state physics. Charged-particle beams from Van de Graaffs to produce unique atomic and nuclear effects, plus X-ray fluorescence and scanning electron microscopy; stable isotope tracers emphasized when radiotracers are not suitable.
78. PHOTOCHEMISTRY OF MATERIALS
IN THE STRATOSPHERE
H. S. Johnston

Study of atmospheric ozone, laboratory and field measurements, interpretation of data, and theoretical analyses; atmospheric accommodation of nitric oxide; photolysis of substances of atmospheric interest, in particular, ozone, nitric acid, nitrogen pentoxide, and the NO$_3$ free radical; atmospheric reaction rates; absorption spectra of atmospheric species; theoretical analysis by the "method of instantaneous rates."

79. RADIATION CHEMISTRY
W. M. Garrison

Specific chemical information on the relative importance of ionic, free-radical and excited molecule reactions involved in the radiolysis of organic compounds with high-energy heavy-ion beams. High linear energy transfer (LET). Use of the 88-inch cyclotron and the Bevalac for the study of LET effects in radiolysis. The $\alpha$-amino acids, $N$-acyl amino acids, and oligopeptides in the solid state and in aqueous solution are compounds being investigated. Studies of radical and molecular product yields in water as a function of LET. Standard chemical dosimetry such as the Fricke and ceric sulfate systems. Basic information for use in the application of high-energy heavy-ion beams in biological and medical research.

80. ENERGY TRANSFER AND STRUCTURAL STUDIES OF MOLECULES ON SURFACES
C. B. Harris

Mechanisms for redistributing the energy in photoexcited molecules into the surface states of metals and semiconductors. Surface sensitive ellipsometry and picosecond laser spectroscopy to follow the primary steps in the redistribution of the energy from photoexcited states on a time scale as short as $10^{-12}$ seconds. Photoelectrolysis. Emission and reflectance spectroscopy of aromatic hydrocarbons adsorbed on transition metal surfaces to characterize changes induced in the molecular and electronic structure of these molecules by physi- and chemisorption.
Spectroscopic studies of transition metal complexes and other systems of interest in catalysis. Study of homogeneous catalysis pertinent to coal-to-liquid fuel technology.

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.

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 a primary information the electronic energy states of the reactants, products, and intermediates. Prediction of the kinetic behavior of complex systems; reactive and nonreactive scattering by hydrogen of a number of ions that appear prominently as contaminants in hydrogen plasmas. Rapid and economical estimation of the energy distributions of the products of some classes of reactions.
84. THEORY OF ATOMIC AND MOLECULAR COLLISION PROCESSES

W. H. Miller

Theoretical studies of the dynamics of chemical phenomena at a molecular level; development of theoretical models and methods to deal with atomic and molecular collision processes. Development and application of a general semiclassical mechanics that allows one to combine classical mechanics and quantum mechanics to describe many features of molecular dynamics. Quantum effects in molecular phenomena and simpler computational methods for carrying out quantitative calculations. The range of application of these various semiclassical approaches includes inelastic and reactive scattering, electronically non-adiabatic collision processes, statistical models for chemical reactions, and most recently semiclassical methods for determining the vibrational states of small polyatomic molecules.

85. PHOTOELECTRON SPECTROSCOPY

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.

86. CROSSED MOLECULAR BEAMS

Y. T. Lee

Investigation of the dynamics of elementary atomic and molecular processes and the energetics of exotic radicals and ion clusters using crossed molecular beams. Information on mechanism and dynamics of chemical reactions obtained from the direct identification and measurements of velocity and angular distributions of product molecules from "single collisions." Reactions of oxygen atoms and free radicals with carbon-containing molecules and radicals under single collision conditions; primary products of many important reactions of oxygen atoms; hyperthermal chemical reactions of hydrogen, deuterium and halogen atoms; reaction of electronically excited atoms and molecules; interaction potentials between atomic and molecular species; inter- and intramolecular energy transfers and the energetics of radical molecules and the spectroscopy of molecule ions.
87. POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS
H. F. Schaefer

Development of new theoretical and/or computational methods for the description of electrons in molecules, with emphasis on the correlation problem, that of formulating models for going beyond the single-particle or Hartree-Fock approximation. Application of theoretical methods to significant problems of broad chemical interest: a) model theoretical studies of chemisorption, metal clusters, and catalysis and b) the potential energy surfaces which govern gas-phase chemical reactions.

88. LOW ENERGY ATOMIC PHYSICS
H. A. Shugart

Research on ion properties (cross sections, lifetimes, and electromagnetic constants), development of a purely-electrostatic ion trap, with possible applications for residual gas analysis, vacuum leak detection, precision spectroscopy, cross-section and ion-molecule reaction studies. Search for universal methods of detecting trace quantities of atoms or molecules; development of an ultra-sensitive, selective method employing coherent forward scattering of light to detect one part in 10^{12}. Laser spectroscopic search for the possible influence of a weak neutral electron-nucleus interaction which would perturb atomic structure; ultraviolet laser development.

89. ATOMIC PHYSICS
R. Marrus

Atomic physics of highly-stripped heavy ions, oscillator strength and wavelength measurements; study of transitions in two-electron atoms of high Z; quenching of the metastable state of Ar^{+17} in an external electric field, study of x-ray transitions using a new method of precision x-ray measurement, search for intense UV transitions in ionized iron and molybdenum elements which are important contaminants of fusion plasmas.
Methods development for utilization of solar energy; green plant photosynthesis; sensitized photodecomposition of water; sensitized photovoltaic devices; hydrocarbons and energy from plants.
91. PHOTOCHEMICAL CONVERSION OF SOLAR ENERGY
   L. Packer

   Biotechnological applications of solar energy: photoelectric potential
generation; catalytic systems in chloroplasts; light-triggered catalysts
in micro-organisms such as cyanobacteria and halobacteria; hydrogen
production by chloroplasts in vitro and production and consumption by
cyanobacteria; applications to artificial convertors.

92. SURFACE CHEMISTRY BY X-RAY PHOTOELECTRON
   SPECTROSCOPY
   T. Novakov

   Study of surface chemistry of materials such as graphite and activated
carbon by x-ray photoelectron spectroscopy, infrared spectroscopy and
laser Raman spectroscopy.
93. FORMATION OF OXYACIDS OF SULFUR FROM SO$_2$  
R. E. Connick  
$30,000  02-01$

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.

94. CONVERSION OF COAL TO CLEAN LIQUID AND GASEOUS FUELS  
G. A. Somorjai, A. T. Bell  
$145,000  02-01$

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 organo-metallic complexes for coal liquefaction; emphasis on developing catalysts to complex aromatic groups and selectively promote reactions with portions of aromatic substrates.

95. SYNTHETIC AND PHYSICAL CHEMISTRY  
W. L. Jolly  
$60,000  02-01$

X-ray photoelectron spectroscopy measurements of atomic core electron binding energies of a wide variety of inorganic and organometallic compounds; interpretation in terms of atomic charges which indicate the nature of the electron distribution and bonding in the molecules. Extent of transition metal d electron "back-bonding" in organometallic compounds. Modes of ligand metal bonding in organometallic molecules. Use of core electron binding to make thermodynamic calculations. Synthesis and characterization of simple but novel compounds of the nonmetallic elements; compounds unstable under ordinary conditions but which can be "trapped" in metastable state and used as reagents in otherwise difficult syntheses.
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.

Oxidation of highly ordered graphite by high-energy oxidizers to make durable and conductive (comparable to aluminum) graphite salts with intercalated anions such as $\text{SO}_3\text{F}^-$, $\text{AsF}_6^-$, $\text{OsF}_6^-$; potential electrochemical anodes. Potentials for redox proton transfer to permit cyclic energy storage. Predict useful paramagnetic and highly conductive cations from multiring aromatics of $\text{Ar}^+\text{X}^-$ formulation useful in synthesis.
98. SELECTIVE HYDROGENATION $183,000 02-01
OF COAL
A. A. Grens, T. Vermeulen

Development of a basis for conversion of coal to liquids; minimum hydrogen addition; selective breaking of certain bond types in the coal structure below pyrolysis temperature; interaction of coals with inorganic and organic reaction media; effects of homogeneous catalysts at moderate temperatures; action of catalyst materials on specific bond types in model compounds; effect of coal pore structure on reaction rates and extents.

99. BIOCONVERSION OF $167,000 02-01
CELLULOSE
C. R. Wilke

Investigation of sugar and ethanol production based on the carbohydrate content of cellulosic materials; hydrolysis of cellulose to sugars and subsequent fermentation to ethyl alcohol; chemical and enzymatic pretreatment of cellulosic materials to remove lignin and hemi-cellulose; enzymatic hydrolysis of α-cellulose to glucose; fermentation of pentoses and hexoses to ethanol; kinetics of enzymatic hydrolysis; continuous process for cellulose enzyme production; adsorption for enzyme recovery; new ethanol fermentation method using a vacuum and dense yeast cultures; form of stored solar energy.

100. CHEMICAL ANALYSIS $100,000 02-03
R. Giauque, R. Clem

Development of trace element analysis methodology for routine use in energy related research: improved x-ray fluorescence trace element analyses. Development of anodic stripping voltammetry and emission spectroscopy; use of ozone as a non-specific oxidant for release of trace metals from sequestering agents, carbon suboxide polymer use to prepare stable graphite anode.

101. TURBULENT COMBUSTION $50,000 02-04
F. Robben

Experimental study of turbulent combustion in the boundary layer of a flat plate: interaction of combustion with turbulence; turbulent flow measurements, time and space resolved measurements of velocity and density. Development of turbulent structures using particle track photography: coherent vortex dynamics in turbulent flows; photography of particle tracer tracks, quantitative measurement of the three-dimensional velocities in a flow field via the hydrogen bubble technique.
Investigation of the scientific feasibility and economic potential of closed-cycle thermochemical processes for producing hydrogen from water using nonhydrocarbon energy sources; identification of at least three promising cycles leading to one or more bench-scale studies and economic evaluations; scientific feasibility and some detailed cycle chemistry established for ZnSe cycle; cycle process design optimization and development of alternative chemical approaches to reduce heat requirements at high temperatures shown to be needed; detailed research on rates, yields, and mechanisms in ZnSe cycle.

The objective of this project is to develop models of the physical and chemical processes in combustion. The models will be tested against existing and future experimental results with the goal of providing a basic scientific resource which can be applied in improving the technology and machinery of combustion. Included are those efforts which form the basic research part of the laboratory's Combustion Research Program.

The work included in this project involves the development of detailed computer code descriptions of the combustion process; their purpose will be to investigate in detail specific mechanisms and experiments in order to provide understanding at the most fundamental level.
Heat pipes offer unique advantages for efficiently carrying heat from one location to another. This effort extends and improves the existing description of heat transfer phenomena in heat pipes in order to achieve improved design codes for high heat transfer rates with liquid metal working fluids at temperatures ranging from 700-1800 K. Substantial revision in heat pipe theory and reformulation of heat pipe design codes is being applied to the development of vertically oriented, gravity assisted heat pipes. Continued theoretical and experimental work is being directed towards improved understanding of transition region, turbulent flow in wick structures, in variable-mass turbulent vapor-phase flow, and in capillary pumping force predictions.
105. RADIATION FROM HIGH TEMPERATURE PLASMAS SEEDED WITH HIGH-Z ELEMENTS
L. 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 neon VI-VIII, nitrogen V, oxygen VI, and line identification and ionization rates for krypton IX-XII. 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.

106. A STUDY OF ENERGY CONVERSION AND TRANSPORT IN SPACE PLASMAS
W. C. Feldman

The solar wind, lower solar corona, and Earth's bow shock magnetopause provide a unique plasma in which any spacecraft approaches a truly nonperturbing diagnostic probe. This effort seeks to make use of existing satellite data to yield information and understanding of plasma and heavy ion physics processes - evolution and saturation of heat flux mechanisms, ion beam and thermal driven anisotropy-driven instabilities, and various sources of the free-energy in particle velocity distributions in the earth's magnetically confined upper atmosphere. Special attention is given to those phenomena which occur in magnetically confined fusion plasmas.
Investigation of sulfur dioxide scavenging from gas streams by means of reversible binding to organometallic substances; development of regenerative scavenging methods; search for substances which bind SO$_2$ as a distinct molecular entity in a labile fashion; chemical bonding similar to hydrocarbon catalysis reactions; coordination of small molecules to transition metals; impact on combustion of high-sulfur coal.
Theoretical and laboratory work to survey thermochemical cycles for hydrogen production from water using heat from nuclear reactors and solar collectors; identification of improved chemical systems; testing of reactions in potential cycles to determine thermochemical parameters, reaction rates, and practical yields; hybrid thermochemical-electrochemical cycles identified which may facilitate processes requiring lower maximum temperatures and less corrosive chemicals.
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.
110. BASIC STUDIES OF HIGH GRADIENT MAGNETIC SEPARATION CAPTURE MECHANISMS
   L. C. Headley, W. H. Simmons, W. F. Lawson, R. P. Treat

Analysis of the dynamics of attraction and capture of magnetic particles by magnetized fibers; separation of sulfur-bearing particles from coal conversion and combustion streams in a high-gradient magnetic field; equation of motion for magnetic particle when acted on by magnetic, viscous, and gravitational forces; particle capture when trajectory intersects the fiber with a favorable static force balance; calculation of trajectories and capture distances for multifiber configurations; experimental determination of trajectories. Inertial terms are included in theoretical equation of motion.
Nuclear Operations Department -02-
R. J. DeSando - Phone: (FTS) 774-3137 or (513) 866-7444
R. A. Schwind - Phone: (FTS) 774-7147 or (513) 866-7444

111. FUNDAMENTAL INVESTIGATION $180,000 02-01
OF METAL-HYDROGEN SYSTEMS
G. C. Abell, R. C. Bowman, Jr.,
J. L. Ivey, C. M. Love

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

112. ISOTOPE SEPARATION $210,000 02-02
RESEARCH AND DEVELOPMENT
B. E. Jepson, E. D. Michaels
W. M. Rutherford

Investigation of isotope separation by liquid phase thermal diffusion and by chemical exchange; multiple column liquid thermal diffusion cascades with annular column spacings of 250 µm and less; thermal diffusion factors (chlorine, sulfur, and bromine isotopes); influence of vertical temperature gradients and coolant hydrodynamics on stability of thermogravitational circulation. Separation of metal isotopes (calcium, lithium, molybdenum, and iron) by chemical exchange with polyethers; countercurrent isotope exchange processes and single-stage separation factors. Derive empirical relations to describe separations in terms of basic parameters.
113. ATOMIC AND MOLECULAR PROPERTIES 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.

114. SURVEY OF ISOTOPE APPLICATIONS

V. L. Avona, R. DeWitt

Survey of current and future applications of isotopes in six general fields: (1) nuclear, (2) agricultural, (3) biological and medical, (4) environmental, (5) geological, and (6) industrial; utilization of uranium and hydrogen isotope separation progress for other elements with little additional research (laser separation and chemical exchange); establishment of priorities for future isotope separation research.
Spectroscopic studies of intermediates present in systems exposed to ionizing radiation and light to provide detail on the molecular and electronic configurations of these intermediates. Examples examined include free radicals, carbenes, radical ions and carbonium ions and excited states of both radicals and neutral molecules. Methods employed include absorption and emission spectroscopy, Raman studies, spectroscopic examination of Stark and Zeeman effects, and optical detection of both electrical and magnetic properties. Many of these studies carried out in doped solids at temperatures down to 4°K to provide the optical resolution required. Vibronic analysis to identify intermediate states present and to understand the electronic transitions involved.

Theoretical studies of the effects of the absorption of ionizing radiation in condensed systems; events which occur in times less than $10^{-9}$ sec. Dynamic properties of electrons produced by radiation; mechanisms for electron localization in solvent traps and reaction with solutes. Role of electron-phonon (vibronic) interaction in addition to that of the structural disorder of the system as localization mechanisms; time-dependent optical absorption spectrum of trapped electrons and its decay pattern; chemical reactions involving localized electrons examined at early times using, in addition to the Smoluchowski equation, the continuous-time-random-walk (CTRW) model of Montroll-Weiss.
117. CHEMICAL PHYSICS OF
REACTING SYSTEMS
J. J. Kozak, M. E. Schwartz

Quantum mechanics, statistical mechanics and non-equilibrium thermodynamics to interpret phenomena and chemical-dynamic processes of interest in radiation chemistry, both at the molecular and macroscopic levels. Electronic structure calculations; model potential methods, self-consistent-field valence bond theory, direct methods for examining ionization phenomena, studies on the conceptual basis of exchange interactions. Theoretical studies of chemisorption, cluster stability, electron-solvent interactions, electron binding energies, photoionization cross sections, spin densities in radicals, and various spectroscopic properties. 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 by an analytical study of the time-dependent Schrödinger equation. Statistical-mechanical theory of electrolytes applied to micellar kinetic processes. Non-equilibrium thermodynamics and non-linear kinetics applied to numerical studies of the cooperative effects associated with examples of coupled chemical reactions.

118. CHEMICAL STUDIES OF
RADIATION INDUCED REACTIONS
R. H. Schuler

Chemical approaches to examine radiation induced reactions; effects of track structure and ion and radical recombination processes on the overall chemistry; liquid chromatographic methods; radiolysis of aqueous solutions; gas chromatography and radio chromatography to examine reactions in organic systems. Computational methods to simulate the course of radiation chemical reactions; effects of the different kinetic variables; effect of solute concentration on product formation (chemical scavenger studies) transformed to give descriptions of the time dependence of intermediates; track and ion recombination processes.
Radiation Laboratory -01- (Continued)

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

Radiation chemical and photochemical effects in micellar systems; catalytic or inhibitive effects of micellar isolation; transport of reaction intermediates across interfacial barriers. Reaction control by aqueous-lipid interface; development of micellar methods to examine kinetic details of chemical reactions; pulse radiolysis and laser photolysis techniques.

120. PHOTOCHEMICAL STUDIES
A. M. Trozzolo

Photochemical studies on organic and inorganic systems to study the mechanism of which absorbed light energy ultimately produces chemical effects. Valence isomerization of heterocyclic compounds; chemistry of photolytically produced biradicals; photochemistry of organometallic compounds and inorganic complexes; electron transfer reactions of singlet oxygen and superoxide anion. Studies on photochromic systems in which a relatively strained heterocyclic ring is either open or closed photochemically to produce a high energy intermediate, whose stability can be controlled, as models for energy storage devices. Biradicals, which are important intermediates in a variety of photo-cleavage reactions of ketones, characterized by direct spectroscopic methods where electron-transfer trapping of these species allows the direct determination of biradical lifetimes. Photochemical studies on organometallic compounds and inorganic complexes for possible efficient photocatalytic systems; electron transfer reactions of singlet oxygen and superoxide anion. A primitive photovoltaic cell based on electron concentration differentials is being investigated.
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. Preparation of a variety of information services including literature searching, preparation of current-awareness aids and bibliographic searching. Bibliographic publications issued regularly are the Biweekly List of Papers on Radiation Chemistry and its annual cumulations and indexes. Evaluated compilations of kinetic and spectroscopic information on reaction intermediates; compilations made available to interested scientists by publication in the NSRDS-NBS series.

Electron spin resonance spectroscopy (ESR) studies of free radical intermediates present in reacting systems in both continuous and pulsed radiolysis and photolysis experiments. Steady state experiments used in situ radiolysis with 3-MeV electrons; intermediates produced by ionizing radiation in organic systems and in aqueous solutions. Time resolved studies using pulsed electron beams to yield kinetic behavior of intermediates on the microsecond time scale and also on chemically induced dynamic polarization of the radicals (CIDEP); spin selective reactions of the radicals; also photochemical experiments using continuous and mechanically and electronically modulated light beams and also with time resolved studies using laser pulses. Data give information on the electronic and geometric structure of radicals such as acidity and rates of protonation and on the rates for electron exchange between radical anions and their neutral parent molecules; data examined and integrated with results from optical studies and chemical approaches to give a more complete picture of the mechanisms of radiation chemical and photochemical reactions.
123. PULSE RADIOLYSIS STUDIES OF RADIATION CHEMICAL REACTIONS
   P. Neta, L. K. Patterson

Kinetic behavior and spectroscopic properties of transient species which absorb light in the UV, visible or near-infrared region by optical pulse radiolysis techniques; processes occurring in the range of $10^{-7}$ to $10^2$ seconds; absorption spectra of the intermediates; time resolution of $10^{-8}$ sec; extension of time resolution of the automated system down to $10^{-9}$ sec. Studies of radiation induced reactions of various organic substrates in aqueous solution; examination of the redox reactions in metal ion-organic ligand complexes with emphasis on examining the cleavage of various inorganic anions and reactivities of the resultant oxidizing intermediates; studies of the effects of local molecular organization on radical kinetics in heterogeneous systems; investigation of the oxidation of organic radicals by electron transfer and determination of the one electron redox potentials of radicals.

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

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 to measure differential scattering of electronically-excited metastable rare-gas atoms by various small molecules (e.g., H$_2$O, CO$_2$, HBr, C$_6$H$_6$, N$_2$, Br$_2$). Time-of-flight techniques to measure the velocities and the identities of the scattered species; detailed information on the cross sections for energy transfer between atoms and molecules; identification of states formed immediately after the initial energy transfer; determination of the potential-energy curves for the interacting atoms and molecules. Examination of the magnitudes and velocity dependences of the integral energy exchange cross sections between excited argon and HBr or CO$_2$ by examining quenching of the differential scattering at large angles; potential-energy curves for the electronically-excited states of atom-molecule complexes to examine the qualitative differences between these and the ground-state curves; effects of the initial relative kinetic energy and of the electronic excitation energy of the atom on the transfer of energy to small molecules.
Properties of very low energy excess electrons in thin-film insulating solids such as rubidium iodide to give information on their transport properties, resonances, and chemical effects; electrons injected from vacuum at known energy, acquire additional energy from the electron affinity of the medium and diffuse through the film; they return to the surface and escape to vacuum unless they lose energy to the lattice of the film or are trapped in a resonant state; electronic structure of the solid (temporary negative ions, excitons, and plasmons) revealed by structure in the current transmitted by the film to a metallic substrate. Examination of optically forbidden transitions; supplemented by correlated measurements of excitation potentials for exciton luminescence. Studies by conventional chemical methods of the decomposition of films under electron bombardment give yield-energy curves to correlate with observed resonances; chemical yields compared with those obtained with gamma-ray irradiations.
Study of reactive intermediates using flash photolysis; reactive free radicals such as H, OH, HO₂, CH₃, CH₃O₂, and CHO. Studies of the reactions of CHO and CH₃ radicals produced by the flash photolysis of H₂O in the presence of CO or CH₄. Determinations of the ultraviolet absorption spectrum of CHO and absolute rate constants for reactions of H with CO, CHO with CHO, and H with CH₃.

Photophysics and photochemistry of processes that may prove useful for the conversion of solar energy into more stable forms, photosynthesis-related and unrelated systems, purified chlorophyll-proteins. Calculation of spectroscopic properties, measurement of electric-field-oriented linear dichroism and fluorescence polarization, and use of cryogenic spectroscopies. Elucidation of the primary conversion mechanisms of photosynthesis by study of the interactions of chemically defined components, including chlorophyll-proteins. The major goal of the photosynthetic-related work is precise definition of the exciton state that immediately precedes the primary "energy storage" state in a photosynthetic reaction center, and insofar as possible use of that avenue to define the storage state itself. Storage of photochemical energy that is recoverable in the form of heat; thermal storage properties of stable photodimers produced from polyacenes in simple solvents.
<table>
<thead>
<tr>
<th>Project Number</th>
<th>Title</th>
<th>Budget</th>
<th>Start Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>128</td>
<td>SURFACE EFFECTS- HYDROGEN RECYCLE CHEMISTRY</td>
<td>$50,000</td>
<td>01-01</td>
</tr>
<tr>
<td>129</td>
<td>ATOMIC AND MOLECULAR COLLISION DYNAMICS</td>
<td>$240,000</td>
<td>01-02</td>
</tr>
<tr>
<td>130</td>
<td>PHOTOCHEMICAL, PYROLYTIC, AND REACTIVE INTERMEDIATES BY ELECTRON SPIN RESONANCE</td>
<td>$150,000</td>
<td>01-02</td>
</tr>
</tbody>
</table>

**128. SURFACE EFFECTS- HYDROGEN RECYCLE CHEMISTRY**

S. H. Overbury

The goal is complete understanding of the processes of energy transfer, chemical reactivity, and re-emission of hydrogen at the first wall of MFE reactors. Apparatus development for study of chemical reactivity of atomic hydrogen with various substrates including isotope effects; study of the hydrogen-carbon system: energy distributions of back-scattered ions, detection of molecular species formed.

**129. ATOMIC AND MOLECULAR COLLISION DYNAMICS**

J. T. K. Cheung, P. F. Dittner, H. F. Krause

Atomic and molecular collision processes including chemical reactivity and intermolecular energy transfer at thermal and epithermal energies; ion pair formation and electron transfer at energies of 1-100 eV; electron transfer, inner shell quasi-molecular effects, penetration phenomena at very high energies. Study of single collision phenomena in atomic and ionic beams using model systems, application to more general systems and to problems of programmatic interest. Apply understanding of electronic excitation in the chemical reactivity of mercury atoms to the reactivity of excited carbon atoms where low lying electronic states are populated at thermal energies; surface and chemi-ionization of UF₆.

**130. PHOTOCHEMICAL, PYROLYTIC, AND REACTIVE INTERMEDIATES BY ELECTRON SPIN RESONANCE**

R. Livingston, H. Zeldes

Chemical free radicals in liquids studied by electron spin resonance; methods of forming radicals include photolysis, pyrolysis, and chemical reaction in molten salts. The radicals with lifetimes ranging down to less than a millisecond observed at steady state concentration as the liquid flows through the spectrometer; radicals identified and features of their electronic structure elucidated. Changes in the nature of the liquid (temperature, pH, solvent, etc.); mechanisms of reactions, motional effects, exchange of protons, pK for ionization, etc.: kinetic studies on the rates of formation and disappearance of radicals. Studies of pyrolytic processes and molten salt solutions and photolytic reactions.
A new program to develop strong capability in theoretical chemistry and to give theoretical guidance and support to the experimental programs including atomic and molecular structure, and chemical reactions. Theory will be used to calculate chemical reaction cross sections, energy distribution in reaction products, potential energy surfaces for atomic and molecular collisions, the structure of molecular fluids, and structures of molecules and ions.
OAK RIDGE NATIONAL LABORATORY

Physics Division

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

132. MOLECULAR RESEARCH WITH $160,000 01-03
ELECTRON SPECTROSCOPY
T. A. Carlson

Development of electron spectroscopy as a useful tool in the study of molecular physics and general chemical behavior; orientation and bonding of molecules on surfaces; combined use of x-ray, uv, and photon-induced Auger spectroscopy to study chemical bonding and spatial orientation; development of ultra high vacuum compatible uv lamp for production of polarized HeI radiation.

133. COLLISIONS OF LOW ENERGY $160,000 01-03
MULTICHARGED IONS
C. F. Barnett, D. H. Crandall

Measurement of electron impact excitation and ionization cross sections for multicharged ions using electron-ion cross beam techniques; charge exchange measurements of low mass ions with atomic hydrogen in the velocity range 0.1 to $1 \times 10^8$ cm/sec; calculation of charge exchange cross sections for energetic ions colliding with hydrogen atoms.

134. HEAVY ION ATOMIC $180,000 01-03
PHYSICS RESEARCH
C. D. Moak, P. D. Miller

Ion stripping in gases and solids; ionic states inside solids; inner shell and outer shell excitation of multiply charged ions; radiative and non-radiative electron capture by multiply charged ions; beam foil spectroscopy and target atom radiation; Auger and auto-ionization processes; stopping powers of heavy ions in gases, solids, and in crystal channels; Coulomb excitation and molecular orbital promotion of atomic states of heavy atoms; electron ejection from solids; quasi-molecular x-ray studies.

135. MOLECULAR INFRARED $120,000 01-03
SPECTROSCOPY
H. W. Morgan

Solid state studies in the infrared spectra region on: the behavior of dopants and impurities, the formation of solid solutions by foreign ions in alkali halide lattices, and the occurrence of solid phase chemical reactions; examination and recalculation of the rotational spectra of small molecules together with Stark effects and energy shifts due to centrifugal distortion; supportive research in the development of submillimeter lasers.
OAK RIDGE NATIONAL LABORATORY
Chemistry Division -02-
O. L. Keller, Jr. - Phone: (FTS) 850-6444 or (615) 483-8611

136. RESEARCHES ON THERMAL
      GENERATION OF HYDROGEN
      C. E. Bamberger, D. M. Richardson

Hydrogen production from water splitting by thermochemical reactions; new
or improved chemical reactions, chemical compounds, thermodynamic data,
and process kinetics to develop viable and economical thermochemical cycles;
minimization of temperatures, work and heat requirements, corrosiveness,
and cost of recycled chemicals; impact on solar energy, synthetic fuels,
and energy storage.

137. AQUEOUS CHEMISTRY AND
      THERMODYNAMICS TO ELEVATED
      TEMPERATURES AND PressURES
      C. F. Baes, H. F. Holmes,
      M. H. Lietzke, W. L. Marshall

Thermodynamics of aqueous systems at elevated temperatures and pressures
for ERDA technological applications using potentiometry, conductance,
isopiestic experiments, and solubility measurements; understanding 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, geothermal chemistry, environmental
chemistry, and processing chemistry.

138. COMPARATIVE INORGANIC
      CHEMISTRY
      D. H. Smith

Fundamental thermodynamic and kinetic information on inorganic systems;
individual system details complemented through comparisons with related
systems; contributions to separations methods. Distribution equilibria
between aqueous solutions and fixed phases (ion exchangers, hydrous oxides,
metal sulfides, activated carbon). Mass transport at interfaces of two-
phase systems, including colloids. Effects of surfactants, micelles,
emulsions; salting effects, including polyvalent counterions.
Adsorption of organics on inorganic solids.
139. HETEROGENEOUS CATALYSIS $145,000 02-01
RELATED TO ENERGY SYSTEMS
   E. L. Fuller, W. C. Waggener
   P. A. Agron, R. A. Strehlow

Model reactions, studied by microreactor with mass spectroscopy and gas chromatography, for understanding and control of non-metallic coal conversion catalysts, commercial and specially prepared. Catalysts studied by ESCA, chemisorption, infrared spectroscopy and gravimetric measurements. Simplified catalyst surface studied by new technique for directional resolution of forces between clean metal surface and adsorbed molecule. Luminescence used to study catalyzed reactions in molecular beams.

140. ORGANIC CHEMISTRY AND THE CHEMISTRY OF FOSSIL FUELS $330,000 02-01
   C. J. Collins, B. M. Benjamin,
   V. F. Raaen, E. W. Hagaman

Identification of "scissile bonds" modified or cleaved in 400° conversion, with hydrogen donor, to preasphaltenes, asphaltenes, oils; better means to attack the bonds leading to coal liquefaction. Investigations with 14C labels of separated vitrinite and of compounds analogous to coal structures. Search for free radical processes. Product identification by gas chromatography, radioactivity assay, proton and 13C nmr spectroscopy.
141. FUNDAMENTALS OF SEPARATIONS $170,000 02-02
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. Difficult-pair separations (Zr-Hf; Ta-Nb) using high pressure liquid chromatography. Continued improvement of process for uranium recovery from wet-process phosphoric acid, and interaction with commercial users.

142. SPECTROPHOTOMETRIC STUDIES $150,000 02-02
OF SOLUTIONS WITH ALPHA-ACTIVE MATERIALS
J. T. Bell, L. M. Toth

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.

143. FLOW THROUGH POROUS $155,000 02-02
BODIES
J. S. Johnson, A. J. Shor

Transport of solutions through packed beds (ion-exchange kinetics), fluidized beds, hyperfiltration and ultrafiltration membranes, and cakes formed in filtration processes; flow instabilities arising from density, viscosity, and interfacial tension gradients in aqueous-hydrocarbon systems (enhanced oil recovery); mass transport effects on microbiological kinetics; impact on nuclear fuel production, waste processing, coal conversion processes; fossil fuel conversion.
Solvation and reactions of polycyclic aromatic hydrocarbons in molten halide hydrocracking catalysts, to determine reaction patterns and origins of catalytic activity. Solvent salts: SbCl₃; AlCl₄⁻–Al₂Cl₇⁻ with inert cations. Substrates contain 2 to 5 fused aromatic rings. Studies of possible salt-hydrocarbon complexation, conditions for protonated and radical cations from neutral molecules; applicability of cyclic voltammetry and electron spin resonance analyses to augment nmr, spectroscopy and quenching.

Basic data needed in development of nuclear reactor fuel reprocessing systems. Development of new chemical processes, solutions to problems arising in existing processes. Identification and study in solvent extraction organic phases of fission product complexes with complexes typically present or intentionally added. Characterization of insoluble particulates encountered in fuel dissolutions in order to mitigate resulting problems. Possible volatilizations during head-end operations. Investigation of techniques to preclude diversion of fissionable material, such as co-processing, seeding with strong gamma-emitters.

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 water (catalysts ferredoxin and hydrogenase) with thermal recycle of reducing substrate or by photooxidation; optimization of reaction rates; isolation, purification and immobilization of necessary enzymes; stabilization of enzymes and substrates; kinetics of redox reactions of ferredoxin.
Evaluation of mass transfer in three-phase fluidized beds for design of coal conversion and biochemical reactors. Investigation of continuous chromatographic system for recovery and purification of relatively large quantities of chemical components. Mechanisms by which very small particles can be agglomerated (difficult solid-liquid separations).

Tritium sorption on yttrium from liquid lithium in static system; investigation of flowing system to reduce the liquid phase mass transfer resistance (impact on fusion reactor blanket). Measurement of equilibrium sorption isotherms for molecular sieves (10A, 15X, and 15Y) at 4.2 to 20°K; cryosorption pumping rates for deuterium, tritium, and helium from fusion reactors.

Origination and investigation of new, potentially useful separations agents and methods and improvement 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 and from weak acids (H₂CO₃, H₂SO₃, H₂S, phenols, carboxylic acids).
Investigation of plutonium losses due to instabilities and solids formation in anticipated LWR reprocessing solutions; plutonium loss mechanisms include precipitates due to zirconium hydrolysis and zirconium-molybdenum and plutonium-molybdenum compound formation; plutonium stripping loss mechanisms in Purex process; formation of polymeric plutonium in reprocessing solutions.
151. RD&D: ADVANCED CHEMICAL MEASUREMENTS TECHNOLOGY
C. Feldman, J. E. Strain, R. W. Stelzner, J. P. Young


152. MASS SPECTROMETRIC RD&D FOR INORGANIC AND ACTINIDES ANALYSES

Development of small-sample analysis using IX-resin beads, applicable (ORNL-IAEA) to energy and to safeguarding. First and second ionization potentials and appearance potentials for lanthanides and actinides. Improved ion sources, ion detection systems (computer-controlled vidicon readout).

153. ION MICROPROBE MASS ANALYZER RD&D: SURFACE CHARACTERIZATION
W. H. Christie, R. E. Eby, R. W. Stelzner

Unique capability in surface analysis, corrosion and diffusion studies, depth profiling, isotopic and elemental analysis. Extreme sensitivity; "semiquantitative" to be improved to quantitative; intercomparison of empirical sensitivity factor data with theoretical thermodynamic model. Dedicated minicomputer to be interfaced for control and data processing. Continued metallurgical studies; effect of adsorbed species on surfaces and relationship to reproducibility; oxide film growth.
154. MASS SPECTROMETRY R&D FOR ORGANIC ANALYSIS

W. T. Rainey, D. C. Canada,
J. C. Franklin

Development of mass spectrometry and separations for identification and quantification of major, intermediate, and trace organic constituents in complex mixtures such as coal liquids and gases. Improved ion sources and associated components; instrumentation and software for data acquisition. MS50/DS50 system: ultra-high resolution, high sensitivity, exact mass measurement. Use of soft ionization techniques (field ionization, low-voltage electron bombardment, energy transfer ionization).

155. ADVANCED SPECTROSCOPIC METHODOLOGY FOR CHEMICAL ANALYSIS

L. D. Hulett, J. M. Dale,
R. W. Shaw, L. Klatt

Development of spectroscopic methods applicable to ERDA programs; design and fabrication of laser-excited opto-acoustic spectrometer for coal and other (opaque, etc.) materials not amenable to conventional techniques. Rapid-scan spectrometry, initially for molecular absorption for liquid chromatography and atomic emissions for gas chromatography. Development of electron spectroscopy (ESCA, Auger, diffraction) for catalyst, corrosion and other energy-related problems. Two new electron spectrometers built for in situ surface studies. Absolute alloy analysis by x-ray fluorescence extended to other samples.
156. STUDY OF THE CHEMICAL BEHAVIOR OF COAL AND ITS RELATIONSHIP TO MODEL COMPOUNDS

J. R. Morrey, G. L. Tingey

Phenolic depolymerization of coal to identify important functional groups, define appropriate model compounds for coal conversion studies. Kinetics (solubility, $^{13}$C NMR) indicate depolymerization followed by slow repolymerization. Nitrogen, sulfur functional groups, current emphasis.

157. A FUNDAMENTAL INVESTIGATION OF HOMOGENEOUS CATALYTIC SYSTEMS FOR THE SYNTHESIS OF HYDROCARBONS FROM SYNTHESIS GAS

J. L. Cox

Investigation of the homogeneous catalytic synthesis of hydrocarbons and oxygenates from hydrogen and carbon monoxide; homogeneously catalyzed hydrogenation of coal with group VIII metals; carbonylation-decarbonylation reactions as possible reversible chain growth-shrinkage mechanisms; decarbonylation of formaldehyde; deoxygenation of carbon monoxide in the presence of polynuclear complexes.

158. THERMOCHEMICAL CONVERSION OF CELLULOSIC WASTES INTO LIQUID FUELS

T. F. Demmitt, P. M. Molton

Investigate chemistry of thermochemical processes for direct conversion of cellulosic materials into liquid fuels; determination of process variables on reaction chemistry and reaction product properties; conversion of aqueous cellulose slurries (with dissolved alkali materials) to liquid fuels; variation of oil yields and properties with temperature (300 to 365°C) and alkali addition; carbon monoxide addition not required to achieve liquefaction; mathematical modeling.
Investigation of hydrogen transfer to coal by hydrogen donor solvents; characterization of photolytic free radical mechanisms; electron spin resonance spectroscopy to identify important intermediates; kinetics and reaction mechanisms of solvent- and coal-derived radicals to form asphaltenes; study reaction of hydroaromatic solvent radicals with acceptor molecules (modified lignin polymer); interaction of solvent and coal-derived radicals with hydrogen.

Development of mathematical models for fluidized and entrained bed reactors in coal conversion processes; prediction of fluidized bed performance as function of size, configuration, chemical reactions, physical changes, and fluidization regimes; fluidization models for macroscopic and individual particle behavior; bubble formation, bubble splitting and coalescence, and effect of bubble wakes and shapes; testing with experimental data; incorporation of individual particle chemical reaction.
161. COMBINED ATOMIC ABSORPTION-MASS SPECTROMETRIC ANALYTICAL TECHNIQUES
J. H. Kaye

Improvement of flameless atomic absorption and mass spectrometric trace analyses through correlation of emitted neutral atoms, ions, and molecular species with nature and temperature of emitting surface; investigation by simultaneous atomic absorption of neutral atoms and mass spectrometric analysis of ionized species.

162. ULTRASENSITIVE LASER-BASED 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, and coherent anti-Stokes Raman spectroscopy; 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.

163. ULTRASENSITIVE RADIOACTIVITY 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; impact on nuclear processing, waste management, nuclear safeguards, and environmental programs.
164. **HEAVY ELEMENT SEPARATION AND ANALYSIS TECHNIQUES**

D. M. Robertson, J. M. Kelley

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

165. **ULTRASENSITIVE MASS SPECTROMETRIC ANALYTICAL TECHNIQUES**

R. L. Gordon, C. R. Lagergren

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 measurement); design, construction, and assembly of a simultaneous mass detection spectrograph; impact on emissions from energy-producing and nuclear waste management processes and measurements for nuclear safeguards.

166. **CHEMICAL CHARACTERIZATION AND MEASUREMENTS TECHNIQUES FOR ENVIRONMENTALLY OCCURRING RADIONUCLIDES**

F. P. Brauer

Development of new sampling techniques and systems for long-lived radionuclides; development of highly sensitive methods for determination of chemical forms and amounts of long-lived radionuclides in environmental and energy-system matrices: iodine-129, tritium, carbon-14, and natural radionuclides; development, testing, and evaluation of methods and materials for selectively collecting various chemical forms in the atmosphere; study and application of new developments in laser-based spectrometry, direct-inlet mass spectrometry and nuclear radiation spectrometry; feasibility of real-time analytical methods.
167. COMBUSTION ANALYSIS BY ADVANCED RESEARCH METHODS

W. T. Ashurst, R. J. Cattolica,
R. A. Hill, D. R. Hardesty,
R. J. Kee, J. A. Miller,
L. A. Rahn, R. E. Setchell,
R. E. Mitchell, J. R. Smith

$195,000 01-02

Advanced research methods, including laser-based diagnostics and new computational schemes, for application to research on combustion processes. Studies of flat flame kinetics and diffusion flame transport using laser Raman, Doppler, and fluorescence techniques; diffusion flame facility for combining several conventional and laser-based diagnostics for the study of turbulent reaction flow; models of those flames with finite rate chemistry and reasonable turbulent transport models. Development of advanced diagnostics including resonance scattering, nonlinear optical and multi-photon techniques.
The information was taken from current 200-Word Summaries provided by the contractors. There is considerable (about 10%) turnover in these research projects and some may not be continued beyond the current contract period.
AEROCHEM RESEARCH LABORATORIES, INC.

201. HIGH TEMPERATURE PHOTOLOYSIS
STUDIES OF COMBUSTION REACTIONS
A. Fontijn - Reaction Kinetics Group

A new program 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. Development of a new experimental technique, high temperature photolysis (HTP) which combines two individually well-tested techniques: (i) the high-temperature fast-flow reactor developed to study the kinetics of metal atom/oxide reactions over about the 300 to 1800 K temperature range and (ii) the photolysis technique used in many laboratories for kinetic measurements of combustion intermediates (free radicals), but only near room temperature. The initial experiments will concern 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 concern reactions of increasing complexity, culminating in radical-radical reactions of higher hydrocarbon and oxidizer radical combinations.

AEROSPACE CORPORATION

202. EXPERIMENTAL STUDY OF
IMPORTANT PARAMETERS IN
TWO PHOTON (TWO-STEP)
ISOTOPE ENRICHMENT
P. F. Zittel - Chemical Physics Department

Investigation of a two-photon isotope separation technique using an infrared laser to vibrationally excite molecules and an ultraviolet laser 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.

BEND RESEARCH, INC.

203. COUPLED TRANSPORT MEMBRANES
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 immiscible organic liquid complexing agent. A basic parametric study including both cation and anion transport, however, it will concentrate at first on anion transport using principally uranium.
204. PHOTO-INDUCED ELECTRON TRANSFER REACTIONS ACROSS PHASE BOUNDARIES
   S. J. Valenty, G. L. Gaines - Chemistry Laboratory, Research and Development Center, Schenectady, N.Y.

Experimental studies of photo-induced 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 Cr(III) analogs of Ru(bipy) complexes in both water soluble and surfactant forms; study of the luminescence quenching of Ru and Cr complexes as water soluble and surfactant derivatives in water and inorganic solvents; study of the luminescence quenching of surfactant complexes in monolayers at the air-water interface; transfer of monolayers to glass supports and study of luminescence on such films; testing of promising systems and configurations for their ability to dissociate water.

205. STUDY OF PHOTOCHEMICAL EFFECTS USING STABLE SEMICONDUCTOR ELECTRODES
   R. H. Wilson, L. A. Harris, R. H. Wentorf, Jr. - Energy Sciences Branch, Research and Development Center, Schenectady, N.Y.

Studies in which a new technique for investigating layers of organometallic compounds will be evaluated. The material to be investigated will be deposited on the surface of stable semiconductor electrodes of known behavior. The semiconductor will be excited by light of sufficient energy to produce bandgap transitions and this energy will be transferred via minority carriers to the surface coating. Initially, previously investigated compounds, such as chlorophyll-a and ruthenium tris-bipyridyl, will be examined using lower energy light for comparison with previous results. The measurements will than be extended with the new techniques using higher energy light.
206. HIGH TEMPERATURE CHEMISTRY OF HYDROGEN PRODUCTION CYCLES
D. L. Hildenbrand - Physical Sciences Division

This research 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$_2$O$_3$ affect significantly the decomposition pressure of MgSO$_4$. The proposed 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.

207. THERMODYNAMICS OF SULFUR ADSORBATES ON METAL CATALYST SURFACES
H. Wise - Materials Research and Catalysis Laboratory

This research is to establish the upper limit of sulfur-bearing compounds in the gas phase, above which deactivation of a given catalyst begins and below which catalyst reactivation becomes feasible. The emphasis of this research is the measurement of the thermodynamic properties of the metal surface-gas interface for sulfur chemisorbed on supported iron, cobalt, nickel and copper catalysts as well as on selected single-crystal faces of these metals.
Compilations of chemical reaction rate data required for modeling of combustion systems. Rate constants for reactions occurring in combustion systems collected, reanalyzed and tested in terms of theory, agreement between laboratories and validity of method to determine most reliable values. Tabulation and distribution of results.

The objective of this work is to provide basic atomic quantities in support of the national Magnetic Fusion Energy Program; effects of minute quantities of heavy ion impurities in magnetically confined plasmas, which are released by wall bombardment; highly ionized species of a number of heavy metals. Development of new theoretical concepts and procedures which specifically include the important relativistic effects for such species; analysis of the regular behavior of atomic quantities along isoelectronic sequences; resonance lines and other prominent transitions of alkali-like and alkaline-earth-like ions. Line strengths for transitions of hydrogen-like species calculated on a fully relativistic basis; many new oscillator strength data on the lithium isoelectronic sequence up to very highly charged species; transition probability data critically evaluated and compiled on the elements V, Cr and Mn.
210. STUDY OF THE CATALYTIC METHANATION REACTION OVER WELL-CHARACTERIZED NI CATALYSTS
J. T. Yates, T. E. Madey, R. D. Kelley,
N. E. Erickson - 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.

211. THEORETICAL RESEARCH IN PHYSICS OF HIGHLY IONIZED HEAVY ATOMS
D. W. Norcross - Laboratory
Astrophysics Division

Use of a model potential approach to the calculation of energy levels and radiative transition probabilities for highly ionized heavy atoms are reported; calculations carried out for eight ions in the sodium isoelectronic sequence from Mg II through W LXIV. The technique involves the solution of the Dirac equation for the single outer valence electron, with a model central potential in the region of the atomic core; the effect of core polarization incorporated in the model potential. The results, for both energy levels and radiative transition probabilities, are encouraging and suggest that the model potentials and wave functions obtained will be quite satisfactory for subsequent calculations of electron impact excitation of these ions.
UNIVERSITY OF ALABAMA

212. ELDOR INVESTIGATIONS OF RADIATION PROCESSES
     L. D. Kispert, T. C. S. Chen - Chemistry Department

Role of a host lattice in determining the type and yield of radicals produced by x-irradiation of a crystalline material as a function of temperature; heavy atom substitution techniques, x-ray crystallography and magnetic resonance measurements, electron-electron double resonance (ELDOR), electron-nuclear double resonance (ENDOR), and electron spin resonance (ESR).

UNIVERSITY OF ARIZONA

213. CHELATING EXTRACTANTS OF IMPROVED SELECTIVITY
     H. Freiser - Department of Chemistry

Development of chelating extractants by application of pattern recognition techniques to the existing data base of metal chelate stability and extraction equilibrium constants; determination of extraction characteristics of selected alkylated 1,2-dihydroxybenzenes and salicylic and phenylarsonic acids with La(III), Th(IV), and U(VI); design of more selective reagents; use of high pressure liquid chromatography to determine fundamental extraction equilibrium and kinetic parameters.

BAYLOR UNIVERSITY

214. RADIATION CHEMISTRY OF HIGH POLYMERS
     M. Dole - Chemistry Department

Study of the kinetics of the radiation-induced crosslinking process of polyethylene by means of electron spin resonance measurements of the decay of the highly reactive free radicals produced by gamma radiation. Polyethylene treated so as to produce single crystals, extended chain crystals, etc.; kinetics of the decay in these different forms of the PE of the two different types of free radicals produced by the irradiation and by transformations subsequent to the irradiation interpreted in terms of a fast and a slow decay process, with or without diffusion control.
UNIVERSITIES

BOSTON UNIVERSITY

215. INVESTIGATION OF THE $52,974 01-01 TRIPLET STATES OF CHLOROPHYLLS
R. H. Clarke - Department of Chemistry

The characterization of the structures assumed by chlorophyll molecules upon aggregation in photosynthetic systems is important for an understanding of the mechanisms of energy conversion in photosynthesis. Since the properties of the excited triplet state of the pigment molecules, such as the electron distribution and excited state dynamics, are sensitive to the surrounding interactions and to the state of aggregation, triplet state properties, serve as a convenient (non-destructive) probe into the makeup of photosynthetic systems. Our research program utilizes optical detection of magnetic resonance spectroscopy to investigate the triplet state properties of the isolated molecule and solutions of aggregated chlorophylls. These measurements allow an evaluation of in vitro chlorophyll systems for structural features proposed as models for the antenna and reaction center of photosynthetic systems in vivo and for their general applicability as model systems for photosynthesis.

216. ELECTRON TRANSFER $55,714 01-01 REACTIONS OF EXCITED DYSES WITH METAL COMPLEXES
N. N. Lichtin, M. Z. Hoffman - Chemistry Department

Study of factors which determine the 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, sensitization, and the influence of solvent and solution composition on dynamic and steady state properties. Objective is to provide a rational basis for selecting photoredox systems for incorporation in photogalvanic solar cells; identify combinations of dyes, metal complexes, sensitizers and solution composition which possess properties consistent with efficient photogalvanic conversion of solar energy; laser flash photolysis; conventional flash photolysis; dynamics of photoredox reactions involving thiazine dyes and complexes of iron as well as of corresponding ground state back reactions.
BOSTON UNIVERSITY (Continued)

217. ORGANIC PHOTOCHEMICAL STORAGE OF SOLAR ENERGY
       G. Jones, II - Department of Chemistry

Study of organic photochemical reactions with the capability of converting solar energy into chemical energy: study of valence isomerization of hydrocarbon dienes induced by visible-absorbing photosensitizers which are electron acceptors; similar work with norbornadienes and visible-absorbing electron donors; study of luminescence quenching and its role in donor-acceptor interactions; role of charge transfer complexes in valence photoisomerization; reactivity of caged valence isomers in the presence of catalysts; development of photocolorimeter for measurement of heats of photoisomerization; use of photocolorimeter to get thermochemical data for unstable molecules.

BRANDEIS UNIVERSITY

218. PHOTOCHEMICAL REACTIONS OF COMPLEX MOLECULES
       IN CONDENSED PHASE
       H. Linschitz - Chemistry Department

Elucidation of the sources of inefficiency in photo-redox reactions involving electron or H-atom transfer to or from light-excited molecules. Laser flash photolysis and luminescence used to observe each stage of the overall redox process; reaction rates and products and intermediates yields allow identification of energy-storing and energy dissipating processes. Correlations made with solvent structure and polarity, redox potentials and nature of excited states. Test substances include metalloporphyrins, including chlorophyll, and aromatic ketones.
BRANDEIS UNIVERSITY (Continued)

219. HYDROGEN TRANSFER AND CHARGE TRANSFER IN PHOTO-
CHEMICAL AND RADIATION INDUCED REACTIONS
S. G. Cohen - Chemistry Department

$33,834 01-01

Electron transfer and hydrogen transfer caused by absorption of ultraviolet or visible light are studied. Reaction of photoexcited carbonyl compounds with amines and other electron donors; sulfur compounds—mercaptans, thioethers and disulfides; quenching of excited carbonyl compounds. Quantitative study of quenching and formation of radicals from reaction of photoexcited carbonyl compounds and dyes with alcohols, amines and sulfur compounds, and on the effects of sulfur compounds in retarding and enhancing reactions in the other systems. Results will be compared with analogous systems subjected to high energy $^{60}$Co gamma radiation and to peroxides.

BROWN UNIVERSITY

220. EXPERIMENTAL CHEMICAL KINETICS
A STUDY OF CHEMICAL REACTIONS BY MEANS OF MOLECULAR BEAM TECHNIQUES
E. F. Greene - Chemistry Department

$59,974 01-02

Inelastic scattering of atoms by diatomic molecules; CsI + Ar and CsI + Xe systems; study of effect in which at low densities neutral atoms and molecules are trapped by a beam of electrons and move preferentially parallel to its direction; details of the interaction; possible practical application in increasing the sensitivity of mass spectrometers and detectors for molecular beams. Measurements of angular distributions of atoms elastically scattered off of crystal surfaces to show features of the structure of the surfaces.
UNIVERSITY OF CALIFORNIA/DAVIS

221. NUCLEAR METHODS IN CHEMICAL KINETICS $55,000 01-01
   J. W. Root - Department of Chemistry

Experimental chemical kinetics investigations of low-energy fluorine and chlorine atom reactions with gaseous hydrocarbons and halogenated hydrocarbons. The information sought includes the relative rapidities of hydrogen abstraction and olefin addition reactions and the effect of temperature upon these relative reaction rates. An unusual aspect of this research is that radiotracer techniques are exclusively utilized in order to prevent the occurrence of severe experimental complications that would otherwise result from the extreme reactivities of atomic and molecular fluorine reagents.

UNIVERSITY OF CALIFORNIA/IRVINE

222. INTERMOLECULAR ELECTRONIC ENERGY TRANSFER PROCESSES $46,358 01-02
   E. K. C. Lee - Chemistry Department

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/exciplex formation, isotope effect, reactive intermediates, long and short range interactions, etc., will be studied by luminescence spectroscopy and chemical kinetics.
UNIVERSITY OF CALIFORNIA/IRVINE (Continued)

223. RESEARCH IN CHEMICAL KINETICS

F. S. Rowland - Department of Chemistry

Research on the photochemistry of chlorine compounds, particularly those found in the earth's atmosphere. Ultraviolet cross sections and reaction rates with O(1D) atoms are being measured for many different halocarbons, and for subsequent decomposition products including CClFO, CF2O, ClONO2 and BrONO2. The photochemistry of ClONO2 is being studied at 302.5 nm. Heterogeneous decomposition reactions are also being studied for ClONO2 and other chlorinated species.

Fundamental reaction rate studies of chlorine atoms are being made with the radioactive 38Cl atoms thermalized by multiple collisions with CClF3. Substrates for 38Cl reaction include several alkenes and alkynes and some organometallic compounds. Intramolecular chlorine atom shifts are being studied with C2H5Cl and C3H4Cl. The rates of hydrogen abstraction by 38Cl are being measured indirectly through competition with vinyl bromide. The method is being extended to 240-360°K.

Fundamental fluorine atom reactions are being investigated with 19F atoms. Substrates include alkenes and alkynes with emphasis on isotopic differences. The effects of radiation damage at high fast neutron flux are being studied.

Studies have been initiated on the reactions of energetic recoil tritium atoms with graphite and lithium chloride.

224. STUDY OF ISOTOPIC MASS EFFECTS IN CHEMISTRY

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.
UNIVERSITIES

UNIVERSITY OF CALIFORNIA/LOS ANGELES

225. CHEMISTRY OF HYDROCARBON SOLIDS AT HIGH PRESSURES
M. F. Nicol - Chemistry Department

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.

226. MECHANISMS OF ENERGY TRANSFER AND PHOSPHORESCENCE-MICROWAVE MULTIPLE RESONANCE TECHNIQUES
M. A. El-Sayed - Chemistry Department

Development and application of phosphorescence microwave double resonance (PMDR) to follow the path of energy flow in a molecule and thus determine the mechanism of the energy transfer processes involved in the intramolecular energy conversion. The method determines the direction of the spins of triplet molecules formed by energy transformation of the excited singlet states formed by light absorption. The method is applied to a number of aromatic hydrocarbons and their halogenated derivatives, nitrogen heterocyclics, and aromatic carbonyl compounds. The dependence of this conversion process on the type of electronic states involved, the molecular structure, the effects of vibrations and the solvents are all being examined.

227. MULTIHETEROMACROCycles THAT COMPLEX METAL IONS
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.
Direct charge exchange between individual ions is expected to be the principal loss mechanism and limiting design factor in any heavy ion driven inertial fusion energy production scheme. Estimates are required of the direct charge exchange cross sections between singly ionized heavy elements in the keV energy range. This project supports calculations using a semiclassical impact parameter approach using independent particle basis functions. The method will be used to calculate charge exchange cross sections for singly charged ion species helium and lead in the 5-50 keV energy range and these results compared with those obtained by other methods.

Studies of the cross sections and emission spectra of metastable rare gas chemiluminescent and excitation transfer reactions; the reactions take place in crossed molecular beams under single collision conditions, permitting definitive identification of primary products. Initial emphasis on reactions of metastable krypton and xenon producing halide excimers with emission spectra in the visible and ultraviolet regions.
A quantitative spectroscopic investigation will be made of the role played by free radical sulfur intermediates in the combustion of sulfur bearing fuels.

Previous experimental difficulties will be overcome by applying new absorption and fluorescence techniques. The former of these is based on gain measurements of a radiating system when placed in a laser cavity and relates to the absorption in the system. By this means, absolute concentrations of $S_2$, SH and CS will be obtained for the first time in flames. In addition, the concentrations of S, S$_2$, SO, SH, CS, and SO$_2$ will also be measured using recently developed fluorescence techniques. Being able to monitor some of the species by both techniques provides a powerful built-in self consistency check. Coupled to more conventional emission measurements of $S_2$, SO, SH, CS and the SO+O continuum, a measure of both ground and electronically excited state populations will emerge.

Studies will be made using two separate laboratory combustion systems designed for reduced pressure and atmospheric pressure flames. These currently available burners will be used to examine hydrogen and propane/air flames containing trace additions of H$_2$S or thiophen, C$_4$H$_4$S.

Studies of transition metal carbonyl compounds which may be suitable for use as homogeneous catalysts in supported liquid phase systems: investigations of homogeneous, solution phase catalysts for the production of hydrogen from water via the water gas shift reaction; exploratory studies to identify active systems; characterization of reaction kinetics and mechanisms; testing for practical application as a supported liquid bed catalyst in fixed bed flow reactors.
UNIVERSITIES

UNIVERSITY OF CALIFORNIA/SANTA BARBARA (Continued)

232. MASS TRANSFER AND CHEMICAL REACTION OF GASEOUS SPECIES IN NON-CATALYTIC AND CATALYTIC POROUS MEDIA SUPPORTING CATALYTIC AND NON-CATALYTIC LIQUIDS
R. G. Rinker - Department of Chemical and Nuclear Engineering

Investigation of homogeneous organometallic catalysts dissolved in non-volatile liquids supported as thin films on porous solids; immobile catalyst with high contact area and free molecular motion; liquid partitioning agent for selective absorption of gaseous reactants; valence isomerization of quadricyclene to norbornadiene with cobalt tetraphenyl porphyrin catalyst dissolved in 1-chloronaphthene on alumina pellets; water-gas shift reaction; decomposition of formic acid vapor; steady-flow diffusion cell; impact on hydrogen production.

UNIVERSITY OF CALIFORNIA/SANTA CRUZ

233. PHOTOINDUCED ELECTRON TRANSFER IN MIXED ORGANIC-INORGANIC SYSTEMS
G. S. Hammond - Division of Natural Sciences

Absorption of light by molecules produces electronically excited states. These excited states have much enhanced reactivity as electron acceptors and electron donors and react with other substances by electron transfer. The products of these photoinduced electron transfers are high energy substances. If the energetic products can be separated even briefly from each other it may be possible to cause them to undergo still further changes which will result in storage of the light energy in usable form. One form of storage might involve reaction of the high energy photo products with electrodes to produce photo-potentials and enable storage as electrical power. Studies of the efficiency of the primary electron transfer reactions, the efficiency of first-formal reaction products and the transport of high energy photoproducts to suitable electrodes are being pursued.
234. STUDIES IN CHEMICAL DYNAMICS $128,275 01-01
A. Kuppermann - Division of Chemistry

Study of molecular collisions: energy flow; determination of intermolecular forces and cross sections; energy-loss spectra; angular distribution of molecular photoelectrons; angular distributions in elastic, inelastic and reactive scattering. Study of the effect of photon energy on the photochemistry of important molecules including UF₆. The unifying goal of these studies is the understanding of the effect on a molecule of a collision with an electron, a photon, or another molecule.

235. APPLICATION OF ION CYCLOTRON RESONANCE SPECTROSCOPY, PHOTOIONIZATION MASS SPECTROSCOPY AND PHOTOELECTRON SPECTROSCOPY TO STUDY THE PROPERTIES AND REACTIONS OF IONS IN GASES $40,000 01-01
J. Beauchamp - Division of Chemistry & Chemical Engineering

Experimental methods of atomic and molecular physics, including ion cyclotron resonance spectroscopy, photoionization mass spectrometry and photoelectron spectroscopy; properties, reactions and photochemistry of metal ions and their complexes in the gas phase; transition metal ions; metal hydrides for information such as metal-hydrogen bond dissociation energies and the cross sections for photoproduction of atomic and molecular hydrogen. Ionic processes occurring in ultraviolet rare gas eximer lasers are characterized to facilitate complete modeling of these devices; data include parameters such as the ionization potential of KrF* and the photodestruction cross sections of atomic and diatomic halogen anions. Photoelectron spectroscopy is being developed as a technique for detecting, characterizing, and monitoring transient species such as excited states and free radicals which are produced in high energy environments.
236. BASIC STUDIES OF ATOMIC DYNAMICS
   U. Fano - Department of Physics

Quantum-physical study of the conditions that favor and control atomic shifts, i.e., chemical reactions. More specifically, studies of the joint motion of electrons around atoms, the joint motion which binds electrons into molecules and hence controls their rearrangements. Past studies have been concerned with atoms of helium and hydrogen molecules. A tentative interpretation of the mechanism by which electrons dislodge one another and thus loosen chemical bonds has been outlined; these ideas are not yet formulated into a mathematical theory.

237. SYNTHESIS, CHEMISTRY AND ANALYTICAL ACTIVITY OF COMPLEXES OF LANTHANIDE AND ACTINIDE METALS IN UNUSUAL OXIDATION STATES AND COORDINATION ENVIRONMENTS
   W. J. Evans - Department of Chemistry

Investigations of the synthesis of several new classes of lanthanide and actinide complexes to enable development of a more comprehensive understanding of the f orbitals which should participate in unusual catalytical transformations specific to these metals. The research is directed toward the synthesis of low and zero valent metal complexes. Examination of the reductive chemistry of these metals to develop basic information concerning the interaction of the lanthanide and actinide metals in a variety of oxidation states with ligands such as phosphines, arsines, cyanide, isonitriles, silyls, stannyls, and olefins. Application of several modern synthetic inorganic reaction techniques including electrochemistry, metal atom vaporization, activated metal synthesis, and crown ether methodology. Elaboration of the reaction chemistry of the new molecular classes with particular emphasis on the potential of the low valent species to participate in new catalytic reactions, reactions for which no precedent exists in transition metal chemistry.
CORNELL UNIVERSITY

238. HYDROGEN CYANIDE REACTIONS IN COMBUSTION SYSTEMS $35,000 01-02

W. J. McLean - Sibley School of Mechanical & Aerospace Engineering

Studies of the chemical processes associated with hydrogen cyanide in combustion environments by the use of a single pulse shock tube with product analysis by gas chromatography. A high temperature fast flow reactor is also used with product analysis by quadrupole mass spectrometry. The two techniques make possible observations spanning a wide range of reaction times and temperatures; comparison of measured compositions with predictions based on plausible models for the reactions.

UNIVERSITY OF DELAWARE

239. AUGER AND REACTION STUDIES OF POISONING BY SULFUR AND REGENERATION OF METAL SYNTHESIS GAS CATALYSTS $84,000 02-01

J. R. Katzer - Department of Chemical Engineering

Studies of the extent and mechanism of sulfur poisoning of metal synthesis gas conversion catalysts, particularly nickel methanation catalysts. Methods of inducing sulfur tolerance in methanation catalysts are being explored and methods of regenerating sulfur-poisoned catalysts are being developed. New surface analysis tools (Auger electron spectroscopy) are being used to measure surface sulfur concentrations and relate them to catalytic activity.

DREXEL UNIVERSITY

240. PHYSICAL AND CHEMICAL STUDIES OF CHLOROPHYLL IN MICROEMULSIONS $32,000 02-01

R. A. Mackay - Department of Chemistry

Studies of the properties and reactions of absorbers in microemulsions, using chlorophyll as a model absorber. Of interest is the physical state of the chlorophyll as well as the chlorophyll mediated photoredox reactions and the factors leading to increased quantum yields. Initial interest is in the study of chemical reactions and interactions at the oil-water interface in microemulsions in order to understand the role of water soluble cofactors.
Characterization of primary physical and chemical steps, as well as secondary chemical reactions, which lead to formation of observed products in the gamma or pulsed electron irradiation of simple gas phase systems; chemical analysis for net products in the presence and absence of reactive chemical additives (free radical scavengers); effect of physical variables such as pressure, temperature, and radiation dose; and comparison with other modes of activation (photolysis, electron bombardment in the mass spectrometer) in order to shed light on primary processes. Studies of the radiolysis of H₂-CO mixtures as well as hydrocarbon-O₂ systems related to interest in synthetic fuels; radiolysis of chlorofluoromethanes is motivated by the atmospheric Freon problem, and studies of systems containing CF₃I and CH₃I are suggested by chemical laser work.

Reactions of high energy species generated in events involving the absorption of energetic quanta, or fast moving charged particles; excited ions, excited molecular species, free radicals and hot atoms. Systems under study include (1) molecular ions of moderate complexity whose unimolecular dissociation characteristics depend on activation by collision with metallic surfaces. The role of molecular structure in determining the fragmentation pattern is of especial interest. (2) ordered and disordered solids which in the reactivity (rates and mechanism) of large free radical species is being investigated using a variety of esr techniques. (3) gas phase aromatic hydrocarbons whose reactivity with photochemically generated OH-radicals is being investigated using a combination of photochemical and mass-spectrometric techniques in a continuous flow system. Attention is focused on end-product analysis in order to allow better interpretation of existing kinetic data.
GEORG WASHINGTON UNIVERSITY

243. LANTHANIDE IONS AS SENSITIVE PROBES IN ENERGY TRANSFER AND ORGANIC PHOTOCHMISTRY
N. Filipescu - Department of Chemistry

Mechanism of energy migration and properties of electronically excited sensitizers, lanthanide ions, competition between phototransformation and energy transfer. Methods of study: spectroscopy (UV-visible absorption and emission, electron spin resonance, nuclear magnetic resonance, time-lapse spectrometry). Points of interest: donor-acceptor energy level matching, rate constants of fundamental steps, dependence of energy transfer on donor-acceptor separation and orientation, electrostatic interaction, correlation of theoretical quantities with experiment. Rate constants for energy transfer for organic donor--lanthanide ion acceptor systems; statistical models for exchange transfer; rigid model molecules have been synthesized and the energy studied spectroscopically and photochemically; esr spectra of new long-lived free radicals were interpreted by use of computer simulation; spectral properties of many hydroxycarbocations and their photorearrangements; energy transfer between cations.

UNIVERSITY OF GEORGIA

244. TRANSITION METAL CHEMISTRY UNDER HIGH CARBON MONOXIDE PRESSURE: AN INFRARED SPECTROSCOPIC STUDY OF CATALYSIS IN THE FISCHER-TROPSCH REACTION
R. B. King, A. D. King - Department of Chemistry

Development of transition metal compounds to catalyze the synthesis of hydrocarbons from carbon monoxide and hydrogen; high pressure infrared spectroscopic cell for reactions and product analyses; simulation of the gas mixtures used for the Fischer-Tropsch synthesis of hydrocarbons from coal; exploration and systematization of metal carbonyl chemistry at high carbon monoxide pressures for possible catalytic activity; study of cluster metal carbonyl carbides.
245. FUNDAMENTAL STUDIES OF SEPARATION PROCESSES
   L. B. Rogers - Department of Chemistry

Investigation of chromatographic systems at elevated temperatures and pressures; faster chromatographic methods for analyzing 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.

246. A STUDY OF MECHANISMS OF HYDROGEN DIFFUSION IN SEPARATION DEVICES
   M. H. Lee - Department of Physics & 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.

247. THEORETICAL STUDIES OF HIGHLY IONIZED SPECIES
   A. Dalgarno, G. Victor - Harvard College Observatory

Development of ways of calculating from first principles the relevant properties of highly ionized atoms for which few experimental data are available; the method developed, relativistic random phase approximation, accounts for an important part of the electron-electron interactions in the ion and includes relativistic effects in a direct way; it is being applied to many important ionic species. For less highly ionized atoms, accurate calculations using a different method, the model potential method, are being carried out in order to obtain a good understanding of the accuracy of the RRPA theory. Transition probabilities and excitation frequencies and wavelengths obtained for several energy levels of essentially all the members of the helium, beryllium and magnesium isoelectronic sequences. A simple formula for extending charge transfer cross sections of highly ionized systems has been obtained. Theoretical studies to identify the most important atomic and molecular processes that affect the energy balance of an ionized plasma. Development of simple generally applicable formulas that can be used to extrapolate from experimental measurements to a wide range of atomic systems; recombination mechanisms, particularly in dissociative recombination, which is the main removal process of molecular ions in cool plasmas.
248. THEORETICAL STUDY OF RADIATIVE INTERACTION AND ENERGY TRANSFER PROCESSES OF MOLECULAR AND ATOMIC SYSTEMS
   L.-Y. C. Chiu - Chemistry Department

Theoretical studies of rotational and vibrational energy transfer; cross sections for V-V energy transfer recalculated for the reaction N$_2$(v = 0) + CO$_2$(001) by treating $q_{\text{max}}$ (-1/d) as an adjustable parameter; preliminary results on vibrational overlap between c$_{3\pi_u}^3$(v = 0) and repulsive b$_{3\pi_u}^1$; hyperfine energy expression for vibronic state $K = v_2 + 1$.

249. LASER INDUCED PHOTOLUMINESCENCE SPECTROSCOPY STUDIES OF THE ENERGY DISTRIBUTION OF RADICALS FROM ATOM-MOLECULE REACTIONS
   W. M. Jackson - Chemistry Department

The vibrational and rotational distribution of radicals produced from the reactions of an atom with a stable molecule will be measured using a tuneable dye laser; atoms will be produced with a low intensity flash lamp and the signal detected with a photomultiplier tube and processed with a box car integrator.

250. KINETIC, MAGNETIC AND MÖSSBAUER STUDIES ON PORPHYRIN SYSTEMS
   P. Hambright - Department of Chemistry

Basic coordination chemistry of metal ion interactions with biologically and geologically occurring porphyrin-type molecules; mechanisms of metal addition, removal, exchange, electron transfer and ligation of the metal-porphyrin. Solid state metal complexes interacting with gases (O$_2$, N$_2$, CO, SO$_2$) are probed by magnetic and Mössbauer means. Mechanisms of removing vanadium and nickel porphyrins from oil are studied, in order to give petro-catalysts longer lifetimes. The possibility of using such thermally stable metal-ligand species as efficient catalysts are being explored, as well as much new chemistry on unusual second and third period metals and oxidation states.
UNIVERSITIES

UNIVERSITY OF ILLINOIS/CHICAGO CIRCLE

251. MEASUREMENT OF GAS PHASE REACTION RATES $39,780 01-02
   R. J. Gordon - Department of Chemistry

Study of hydrogen atom exchange reactions, \( \text{D} + \text{HX} + \text{H} + \text{DX} \) 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.

UNIVERSITY OF IOWA

252. THE DISTRIBUTION OF ENERGY IN BIMOLECULAR CHEMILUMINESCENT REACTIONS INVOLVING HYDROGEN $42,000 01-01
   W. C. Stwalley - Chemistry Department

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\(^\circ\)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, Li\(_2\) 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 Li\(_2\) and LiH.

JOHN HOPKINS UNIVERSITY

253. FAR INFRARED CHEMICAL LASERS $55,000 01-01
   D. W. Robinson - Chemistry Department

Rates and mechanisms of chemical reactions in which the energy evolved is specifically located in certain dynamic modes of the products: electronic, vibrational, rotational; inversion of equilibrium energy distributions, chemical lasers; \( \text{OH} + \text{Ar}, \text{HCN} + \text{CO} \) systems.
JOHN HOPKINS UNIVERSITY (Continued)

254. STUDIES IN HOT ATOM AND RADIATION CHEMISTRY
     $60,000  
     01-01
     W. S. Koski, J. J. Kaufman - Chemistry Department

Kinematics and dynamics of positive ion reactions such as Cl+, Br+ and Br+ with molecular hydrogen; Cl+(H2,H)ClH+; reactivity of the ground state and first excited state of the ions; factors that determine the position of the limiting value of the translational exoergicity in the reactions F+(H2,H)FH+ and C+(H2,H)CH+; internal energy distribution in the CH+ product.

UNIVERSITY OF KANSAS

255. STEREOELECTRONIC PROPERTIES $65,000  
     AGGREGATED CHLOROPHYLL SYSTEMS  
     01-01
     R. E. Christoffersen, G. M. Maggiora - Chemistry Department

Quantum mechanical studies of electronic structural features (both for ground and for excited states) of isolated chlorophyll and related molecules; examination of the structure of and forces responsible for the formation of dimeric chlorophyll systems.

KANSAS STATE UNIVERSITY

256. ATOMIC PHYSICS WITH $350,000  
     HIGHLY IONIZED IONS  
     01-03
     P. Richard, J. R. MacDonald - Physics Department

Use of monoenergetic ions in a pure charge state from a Van de Graaff accelerator to study processes of charge exchange (electron loss and electron capture) and ionization for gas targets as a function of the important parameters which include charge state, energy, atomic number and collision distance (impact parameter). These processes are also being investigated in solid targets and, in particular, the charge state fractions of the ions and x-ray yields of the target material are being obtained as a function of the distance into very thin foils (1-500 μg/cm²). These results are important for the proper interpretation of x-ray cross sections obtained from heavy ion-atom collisions in solid samples. The primary process of radiative decay is being investigated with high resolution x-ray spectrometers in order to deduce the final stages of the collision, the fluorescence yields and the state of polarization of the emitted radiation.
UNIVERSITIES -101-

LOUISIANA STATE UNIVERSITY

257. THEORETICAL STUDIES OF EXCESS ELECTRONS IN FLUIDS $42,862 01-01
N. R. Kestner - Department of Chemistry

Theoretical studies and formulation of models for the trapping of electrons in fluids; testing of the models against experimental data. The studies will treat, sequentially, pure solvents, fused salts, mixed solvents and, finally, electron transfer reactions leading to solvated electrons. The methods are those of ab initio and semiempirical quantum chemistry.

258. ELECTRON EXCITATION CROSS SECTIONS FOR MULTIPLY CHARGED IONS $51,657 01-03
J. Callaway, R. J. W. Henry - Department of Physics & Astronomy

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 is from the threshold for excitation to (roughly) 4 times the ionization energy. Cross sections for the electron impact excitation of C$^{3+}$ and Ar$^{15+}$ using a 5 state close coupling expansion and the non-iterative integral equation method of Smith and Henry; electron energies up to three times the threshold energy. Pseudo-state calculation for He$^+$ in which 1s, 2s, 3s and 3p functions are included in a close coupling expansion; 1s → 2s excitation.

MARQUETTE UNIVERSITY

259. SOLID PHASE CATALYSTS AND REAGENTS $40,000 02-01
S. L. Regen - Department of Chemistry

The proposed research is concerned with the development of efficient catalytic methods for accelerating aqueous phase-organic phase reactions and to develop polymer resins which will provide a high degree of selectivity to synthetically important catalysts and reagents. Particular interest is in the development of the triphase catalysis principle. The principal goals of this phase of the work are: (1) developing new forms of solid-phase catalysts, (2) exploration of possible synthetic applications and (3) examination of the detailed nature of the microenvironment within the resin-catalysts. A particular emphasis of these studies addresses the selectivity of these catalyst systems.
UNIVERSITY OF MARYLAND

260. RADIATION-INDUCED EFFECTS IN POLYMERS AND RELATED COMPOUNDS  
J. Silverman - Laboratory for Radiation & Polymer Science

Irradiation of acrylamide-polyethylene and of methacrylonitrile-polyethylene systems to determine the possible sensitization of crosslink formation; measurement of free radical migration in irradiated single crystal alkanes; measurement of the drift mobility of fast negative carriers in irradiated CS$_2$-solutions; measurement of the effect of the filler content on the gel fraction of irradiated polyethylene-filler systems; pulse radiolysis of styrene solutions.

261. NON-DESTRUCTIVE DETERMINATION OF TRACE ELEMENT CONCENTRATIONS  
W. B. Walters, G. E. Gordon, W. H. Zoller - Department of Chemistry

Development of a neutron-capture gamma-ray spectrometer to determine trace-element concentrations in a wide variety of samples; utilization of a large-volume, high-resolution germanium (lithium) detector with a split annulus Compton suppression pair spectrometer; emphasis on high sensitivity and automatic data analysis.

UNIVERSITY OF MASSACHUSETTS

262. DYNAMICS OF, AND HEAT AND MASS 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

263. PHOTOCHEMICAL ENERGY STORAGE: $56,114 01-01
STUDIES OF INORGANIC
PHOTOASSISTANCE AGENTS
M. S. Wrighton - Department of Chemistry

Photoinduced oxidation-reduction chemistry at solid-liquid interfaces; factors controlling rates of photoinduced interfacial electron transfer; evaluation of such primary processes in storage of optical, including solar, energy. Photoinduced charge-transfer processes occurring at irradiated semiconductor electrode-electrolyte interfaces; surface-localized energy levels and electron transfer rate under variable conditions; role of energetics and kinetics in controlling whether given photochemistry occurs.

264. THEORY OF CHEMICAL KINETICS $47,000 01-02
J. Ross - Department of Chemistry

Research on the prediction of the dynamics of reactive collisions: reaction cross sections, disposition of exoergicity of the reaction which is of importance in the formation of energy-rich molecules, relation of reactivity to structure and complexity of the reactants. Search for well-posed approximations to formal collision theory and development of simple theoretical expressions which readily give the dependence on masses (isotope effects), on features of the potential surface, and on properties of reactants and products (vibrational frequencies, etc.); utility of generalized Franck-Condon factors in chemical reactions and energy transfer problems; reactions proceeding by direct interactions, complex formation, and electronic curve crossings; effect of symmetry on heterogeneous (surface) reactions and on reactions in the presence of external fields. Cooperative processes in potentially unstable chemical systems investigated in the rates of growth of colloidal particles.
Photionization and Field

IONIZATION OF HIGHLY EXCITED
ONE- AND TWO-ELECTRON ATOMS
D. Kleppner - Department
of Physics

Experimental studies of the structure of highly excited (Rydberg) states of one and two electron atoms in high electric fields; photoionization processes in atomic species close to their ionization limits. Such species exhibit relatively long lifetimes (compared to those atoms excited in lower levels of excitation) and offer unique opportunities to probe atomic structure and electron correlation phenomena.

Electron Spin Resonance

STUDIES OF RADIATION EFFECTS
M. T. Rogers - Department
of Chemistry

Radiation damage in various classes of organic and inorganic solids produced by γ rays, x rays and ultraviolet light; paramagnetic fragments or defects so identified by ESR and the ESR parameters are used to determine the molecular and electronic structures of the radicals. Temperature and time dependence of the ESR spectra to determine the stability of radicals, their structural and conformational changes, and their chemical reactions; paramagnetic species which are interesting structurally but cannot be prepared chemically in macroscopic quantities. Quantum chemical calculations of radical geometries and electron distributions. Organic materials investigated include carboxylic acids, amides, aliphatic halocarbon derivatives and alicyclic compounds. Inorganic materials studied are metal fluorides, oxyfluorides and cyanides and their paramagnetic products include metals in unusual valence states, excess-electron radicals and hole species; prediction of the nature of radiation damage in non-metallic materials.
MICHIGAN STATE UNIVERSITY (Continued)

267. PROPERTIES OF SOLVATED ELECTRONS, $42,000 01-02
ALKALI ANIONS AND OTHER SPECIES
IN METAL SOLUTIONS AND KINETICS
OF CATION AND ELECTRON EXCHANGE
REACTIONS
J. L. Dye - Chemistry Department

Solvated electrons produced by active metals such as sodium dissolved in
amines and ethers; formation of alkali metal anions; organic "cage-type"
molecules to trap the positive ions and isolate solid compounds which
contain alkali metal anions which behave as semiconductors. Properties
of solvated electrons and alkali metal anions and their potential as
reducing agents for chemical synthesis. Conversion of light energy
into solvated electrons by the sodium anion in solution; absorption of
light by metal anions in solid salts; electrical energy from light
energy by using these newly developed compounds.

UNIVERSITY OF MINNESOTA

268. THE CONTRIBUTION OF ELECTRONICALLY $70,000 01-01
EXCITED STATES TO THE RADIATION
CHEMISTRY OF ORGANIC SYSTEMS
S. Lipsky - Department
of Chemistry

Photophysical properties of organic molecules that have relevance in
determining their radiation-chemical and photochemical behavior:
measurement of rates at which very highly excited electronic states
of simple aromatic molecules non-radiatively dissipate their energy
via cascade to lower electronic states and determination of the
influence of the molecular environment on the magnitude of these
rates; characterization, by fluorescence spectroscopy, of the lowest
excited states of saturated hydrocarbons in order to understand the
important influence of rather minor structural modifications on the
photostability of these molecules; electron-impact spectroscopy to
locate the energies of triplet states of these molecules to better
predict the involvement of such states in photochemical processes
and in the process of energy migration in the liquid phase of these
molecules; measurement of the energy required to eject an electron
from a molecule in a condensed phase and study of the influence of
the nature of the solvent to alter this energy and to alter the overall
efficiency of the ionization process. Absorption and emission properties
of molecular Rydberg states under heavily perturbed conditions such as
exist in a high pressure gas or liquid phase.
269. STUDIES IN CHEMICAL REACTIVITY
R. W. Carr, Jr. - Department of Chemical Engineering & Materials Science

Rates and mechanisms of hydroxyl radical reactions occurring in or related to both combustion and to pollution in the earth's atmosphere; reaction of hydroxyl radicals with propylene by steady-illumination photolysis methods. Fate of CFCl₂ and CP₂Cl radicals produced when the parent species react with hydroxyl radicals in the lower atmosphere. The final environmental disposition of the chlorine and fluorine; removal of energy from highly energetic polyatomic molecules by collisions; collisional deactivation of methylcyclobutane and ethylcyclobutane by cyclobutane and cyclohexane.

270. REACTIONS OF IONS WITH ATOMIC AND MOLECULAR FREE RADICALS
W. R. Gentry - Chemistry Department

Studies of the microscopic reaction dynamics in collisions of ions with atomic and molecular free radicals, importance of electronic non-adiabaticity in chemical reactions. \( \text{H}_2^+ + \text{C}, \text{N}, \text{O}, \text{F} \rightarrow \text{CH}^+ + \text{H}, \) etc. systems, relative kinetic energy from \( \sim 0.002 \) eV to \( > 20 \) eV, using a merged molecular beam apparatus. \( \text{D}_2^+ + \text{X} \rightarrow \text{DX}^+ + \text{D}, \) systematic variations of the reaction dynamics in the series \( \text{X} = \text{C}, \text{N}, \text{O}, \text{F} \) elucidates the reaction mechanisms.

271. CONTINUOUS CHEMICAL REACTION CHROMATOGRAPHY
R. Aris, R. W. Carr, Jr. - Department of Chemical Engineering & 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.
UNIVERSITY OF MINNESOTA (Continued)

272. PHOTO-INDUCED CATAPHORETIC ISOTOPE SEPARATION

J. A. Carruthers, L. M. Chanin, H. J. Oskam - 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

273. THE RADIATION CHEMISTRY OF PLASTIC CRYSTALS

T. J. Klingen - Chemistry Department

Radiation chemistry of the carboranes, adamantanes and organometallic carbonyls in the plastic crystalline solid state; development of a modified diffusional model of the radiation chemistry to fit the liquid-like nature of this solid state of matter. Study of the radiation chemistry of a homologous series of compounds exhibiting the plastic crystalline state; determination of the effect of radiation on the electro-optical properties of various plastic crystals; investigation of the diffusion of radiation-induced impurities in the plastic crystalline state using the positron probe technique.

UNIVERSITY OF MISSOURI/ST. LOUIS

274. OBSERVATION OF LUMINESCENT SPECTRA IN LOW ENERGY ION-NEUTRAL COLLISIONS

J. J. Leventhal - Physics Department

Internal excitation energy of atoms and molecules produced in low energy molecular collisions by observing luminescence emerging from a collision cell containing neutral molecules, into which a beam of positively charged atoms or molecules is directed; spectral distribution of the collision-produced luminescence yields microscopic details of the collision process since only single ion-molecule encounters occur in the collision cell. Determination of internal energy stored in the molecular collision products and the partitioning among the available molecular internal energy levels; efficiency of the conversion of kinetic to internal energy.
275. HALOGEN ATOM REACTIONS ACTIVATED BY NUCLEAR TRANSFORMATIONS
E. P. Rack - Chemistry Department

High energy reactions of halogen atoms or ions, activated by nuclear transformations, studied in gaseous, high pressure and condensed phase saturated and unsaturated hydrocarbons, halomethanes and other organic systems, reactivity of high energy species; effect of collapsing molecular environment on high energy atoms or ions and their reaction channels; systematics of halogen atom reactions, reactions of high energy iodine with olefins and acetylene, the gas to condensed phase transition in all the suitable systems studied, kinetic theory applications and mathematical development of caging mechanisms, stereochemistry of chlorine and iodine substitution reactions involving diastereomeric molecules. Properties of the I₂-acetylene complex compared to those predicted by RRKM, caged complex and caging radical theories.

276. PRINCIPAL PROCESSES IN THE RADIOLYSIS OF GASES WITH FISSION RECOILS AND GAMMA RAYS
G. G. Meisels - Department of Chemistry

Studies of fission recoil behavior in gases: measurements of the quantity of reactive, energetic intermediates procured in the track of a recoiling fission fragment, the microscopic volume in which they are formed, and the extent to which that small volume is heated by the fission recoil over a range of densities. Studies of the formation and reactions of ions with well known internal energies: production of ions by vacuum ultraviolet light of well defined energy and determination of the minimum energies at which ions are formed, as well as the nature of excited states which result at higher energies; determination of the chemical fate of the ions in the absence of other gases (unimolecular reactions); measurement of the rate of reaction when the ions are in thermal equilibrium with surroundings.
277. PHOTOIONIZATION OF ATOMS $59,700 01-03
J. A. R. Samson, A. F. Starace - Department of Physics & Astronomy

Experimental and theoretical study of atomic photoionization processes; cross sections in the vacuum ultraviolet region; effects of electron correlation and of spin-orbit interaction on atomic photoionization processes. Measurement and/or calculation of 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; rare gases and open-shell atoms. Theoretical study of photoionization of hydrogen-like atoms in high laboratory magnetic fields. Rotatable vacuum UV polarizer and fixed electron energy analyzer, measure the photoelectron angular distribution of atomic oxygen at 584 Å; rotatable 127° electron energy analyzer for measurements of photoelectron angular distributions at other wavelengths. Measurements of photoelectron branching ratios across an autoionizing resonance. Construction of a photoionization mass spectrometer system to measure multiple photoionization cross sections.

278. CHARGE TRANSFER CROSS SECTION $31,807 01-03
DETERMINATIONS IN HEAVY ION-HEAVY ION COLLISIONS
J. H. Macek, G. Gallup - Department of Physics & Astronomy

Direct charge exchange between individual ions is expected to be the principal loss mechanism and limiting design factor in any heavy ion driven inertial fusion energy production scheme. Estimates are required of the direct charge exchange cross sections between singly ionized heavy elements in the keV energy range. This project will use the molecular perturbed stationary state approximation method to calculate charge exchange cross sections. The study will assess the need to take into account metastable, intermediate charge states. Results of this technique will be compared with those obtained by other procedures.
UNIVERSITIES

UNIVERSITY OF NEVADA

279. TRIPLET ENERGY MIGRATION AND 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

280. THE PHOTODETACHMENT SPECTRUM OF H-
H. C. Bryant - Department of Physics & Astronomy

Experimental studies to probe the structure of the simplest two electron atom (hydrogen minus) as an important testing ground of atomic physics theories and calculations. Single and double photodetachment measurements using 1.5 to 20 eV photons incident on a relativistic hydrogen ion beam produced by the Los Alamos Meson Physics Facility (LAMPF) in the presence of strong (3 x 10^5 volts per centimeter) electric fields. The number and lifetimes of several excited states as well as the associated Feshbach resonances will be determined.

CITY UNIVERSITY OF NEW YORK/BROOKLYN COLLEGE

281. APPLICATION OF NUCLEAR AND 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. Effects of chemical state on branching ratio electron capture/positron emission radioactive decay; 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.
UNIVERSITIES

CITY UNIVERSITY OF NEW YORK/BROOKLYN COLLEGE (Continued)

282. STUDIES OF CARBON ISOTOPE FRACTIONATION
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.

STATE UNIVERSITY OF NEW YORK/BUFFALO

283. STUDY OF DYE LASER INTRACAVITY ABSORPTION AS A DETECTOR OF LOW DENSITY SPECIES
G. O. Brink - Department of Physics
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.

NORTHWESTERN UNIVERSITY

284. THEORETICAL STUDIES ON HETEROGENEOUS COMBUSTION
C. K. Law - Department of Mechanical Engineering & 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.
285. THE PROPERTIES OF SUPPORTED METAL CATALYSTS
J. B. Butt - Department of Chemical Engineering, R. L. Burwell - Department of Chemistry, J. B. Cohen - Department of Materials Science & 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.

286. KINETICS OF IONIZING RADIATION INDUCED REACTIONS
R. F. Firestone - Department of Chemistry

Chemical and physical mechanisms for formation and destruction of excited rare gas atoms and molecules in rare gases subjected to pulsed high energy electron beams. Procedure consists of (i) passage of electron beam through gas sample for one hundred millionth of one second, (ii) passage of beam of white light through sample for one thousandth of one second following (i), (iii) measurement of light absorbed and/or emitted by excited atoms and molecules. Measurements indicate nature of and provide details of chemical and physical reactions in the rare gas samples. Electron beam generation of highly excited rare gas atoms and atomic ions; secondary reaction population of lowest-lying excited manifold of atomic levels (Paschen 1s); reaction via collisional mechanisms to form the laser molecular level. Efficiency of formation of laser level molecules dependence upon rare gas pressure and purity of sample at pressures in 100 to 1000 torr range.

287. PULSE RADIOLYSIS STUDIES OF FAST REACTIONS IN MOLECULAR SYSTEMS
L. M. Dorfman - Chemistry Department

Chemical kinetics of elementary processes in molecular systems studied by pulse radiolysis; mechanisms by which chemical and biological effects are produced by ionizing radiation. Formation and reactivity of organic molecular ions in solution, with special reference to carbonium ions and carbanions. Rates and mechanism of electron transport in redox proteins; specific rate and mechanism of carbon monoxide uptake by hemoglobin.
UNIVERSITY OF PENNSYLVANIA

288. ANISOTROPIC INTERMOLECULAR $38,000 01-02
INTERACTIONS AND ROTATIONAL ORDERING IN HYDROGEN CONTAINING SOLIDS
D. White - Department of Chemistry

Experimental and theoretical studies of the macroscopic and microscopic behavior of molecular crystals including dynamical processes important in energy transfer: molecular hydrogens and other simple diatomic hydrogen-containing molecules, mixtures of ortho-para species in the solid hydrogens, impurity and isotope effects. Experimental techniques include measurements to 100 millidegrees Kelvin utilizing a $^3$He-$^4$He dilution refrigerator: thermodynamic measurements, pulsed NMR and optical Raman studies.

289. THERMOCHEMICAL PROCESSES $71,535 02-04
FOR HYDROGEN PRODUCTION BY WATER DECOMPOSITION
D. D. Perlmutter, A. L. Myers - Department of Chemical & Biochemical Engineering

Investigation of mass and heat transfer processes, with and without chemical reactions. Involves heat transfer models derived and tested on experimental rotary reactors for solid decomposition process steps; effect of surface renewal of solids on mass transfer; and catalysis by selected additives. These studies are related to thermochemical hydrogen systems including hybrid cycles which combine low-voltage electrolysis and high temperature endothermic reactions.

PENNSYLVANIA STATE UNIVERSITY

290. THE RADIATION CHEMISTRY $46,821 01-01
OF VOLATILE SILANES AND GERMANES
F. W. Lampe - Department of Chemistry

Chemical reactions that are initiated by the passage of radiation through systems containing volatile organo-silicon and organo-germanium compounds. Irradiation by gamma rays; chemical analysis of the products formed under various conditions of pressure and energy-deposition rate results in a picture of the overall chemical conversions induced by the radiation. Detailed reactions and properties of ions and free-radicals derived from silicon and germanium compounds investigated concurrently in photochemical and mass spectrometric experiments.
291. OSCILLATOR STRENGTHS FOR HIGHLY IONIZED ATOMIC SYSTEMS
C. F. Fischer - Computer Science Department

Theoretical study of trends in and calculation of oscillator strengths for atomic systems with one or two electrons outside closed shells, including electron correlations, spin-orbit interactions, and relativistic effects. Focus is on those atomic species of special interest as contaminants in fusion plasmas - lithium and copper isoelectronic sequences.

292. CRYSTALLITE SIZE AND SUPPORT 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 H2 and CO. One objective of the proposed 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 H2 + 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 CH4 formation and maximize the production of olefins and chemical intermediates.

293. MICROWAVE-OPTICAL DOUBLE RESONANCE SPECTROSCOPY
D. W. Pratt - Department of Chemistry

Structure of matter and its interaction with radiation through the exploration of new physical and chemical phenomena; short-lived chemical species produced by irradiation of solids with x-rays, y-rays, and ultraviolet light, and include electronically-excited molecules, free radicals, and collective excitations in solids; optical detection of magnetic resonance spectroscopy.
UNIVERSITY OF PITTSBURGH (Continued)

294. CHARGE EXCHANGE COLLISIONS OF $85,000 01-03
HIGHLY STRIPPED IONS WITH
ATOMIC HYDROGEN
J. E. Bayfield - Department of
Physics & Astronomy

Experimental studies of charge exchange processes between highly stripped ions and between ions and atomic hydrogen. Charge exchange measurements required to assess impurity radiation loss mechanisms and auxiliary neutral beam plasma heating effectiveness in magnetic fusion systems. Charge exchange cross section measurements between carbon, nitrogen, and oxygen ions with charge state plus two to plus six and between these ions and atomic hydrogen using Oak Ridge National Laboratory and University of Pittsburgh accelerator facilities.

PRINCETON UNIVERSITY

295. INELASTIC MOLECULAR COLLISIONS- $28,704 01-02
APPLICATIONS OF THEORETICAL
METHODS TO PROBLEMS IN RELAXATION
PHENOMENA AND LASER OPERATION
H. Rabitz - Department of Chemistry

Aspects of molecular collision phenomena; new theoretical methods capable of handling realistic collision problems; variationally based decomposition methods along with effective Hamiltonian-type techniques; vibrational relaxation of HF; rotational state participation in vibrational relaxation. Modeling of HF lasing under various experimental conditions. Analysis of key physical factors controlling various types of collision behavior; temperature and quantum number scaling of vibration-vibration exchange rates. Chemical reaction theory based on a combination of decomposition methods and special channel coupling techniques; multichannel reactive cross sections.

296. NOVEL ENERGY SOURCES AND $79,603 02-01
ENERGY CONSERVATION PROCESSES
BASED ON CATALYSIS
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.
UNIVERSITIES

PURDUE UNIVERSITY

297. FLASH PHOTOCHEMICAL $57,568 01-01
STUDIES OF TRANSIENT ELECTRODE PROCESSES
S. P. Perone - Department of Chemistry

Photochemical, electroanalytical and spectroscopic studies of the transient phenomena which are characteristic of three types of processes at electrode/solution interfaces, having potential value in solar energy conversion. The three types are photoemission of electrons, photolytic oxidation/reduction of excited species and photosensitized electrolysis at semiconductor electrodes. Formation of solvated electrons when a metallic electrode/solution interface is irradiated, and redox properties of those species that scavenge the solvated electrons. Theoretical modeling of the transient processes complements the experiments. Photoemission in a platinum half-cell with adsorbed chlorophyll aggregates. Role of oxygen as a super-sensitizer for photoreduction of excited dyes at p-type semiconductor electrodes.

298. A FUNDAMENTAL STUDY OF THE MECHANISM AND KINETICS OF CELLULOSE HYDROLYSIS BY ACIDS AND ENZYMES $85,000 02-01
G. T. Tsao - School of Chemical Engineering

Utilization of cellulosic wastes as an alternative source of fuels and chemicals; conversion of cellulose into glucose and fermentable sugar by a two-stage process; acid pretreatment followed by enzymatic hydrolysis; isolation and purification of enzyme components for kinetic studies; activity of enzyme mixtures studied theoretically and experimentally. Studies on cellulose dissolution and separation from lignin.

RICE UNIVERSITY

299. ENERGETICS OF ATOMIC $200,000 01-03
AND MOLECULAR INTERACTIONS
G. K. Walters, N. F. Lane - Department of Physics

Structure and interactions of excited atoms, molecules, electrons and ions in both gases and liquids, as well as properties of and atomic interactions with solid surfaces. Use of electron (e-beam) bombardment and time-resolved spectroscopy in the study of transient excited species in dense gases of laser importance; new approaches to the study of atomically clean crystalline surfaces, and their interaction with ambient gases; development of tuneable ultraviolet lasers; theoretical studies of collision processes involving electrons, ions, atoms and molecules.
UNIVERSITY OF ROCHESTER

300. FUNDAMENTAL STUDIES IN ISOTOPE CHEMISTRY

J. Bigeleisen - Department of Chemistry

Theoretical correlation of isotope effects with molecular and inter-molecular 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.

UNIVERSITY OF SOUTH CAROLINA

301. THE USE OF POLYETHERS IN THE TREATMENT OF ACIDIC HIGH ACTIVITY NUCLEAR WASTES

M. W. Davis, Jr. - Department of Chemical Engineering

Search for crown ether able to extract Cs, Sr (to 99.9%) from nitric acid solution such as nuclear waste into kerosene or CCl₄ containing TBP. Modification of crown ether solubility by means of alkyl chains to reduce aqueous phase solubility.

STANFORD UNIVERSITY

302. RESONANCE ABSORPTION SPECTROSCOPY OF COMBUSTION GASES USING DIODE LASERS

R. K. Hanson, C. H. Kruger - Department of Chemical Engineering

A tunable infrared diode laser will be used to perform high resolution spectroscopy on combustion gases. Initially work will focus on measurement of NO and CO, species of interest in combustion research, using a flat flame burner.
UNIVERSITY OF TENNESSEE

303. RESEARCH CONCERNING IONIC AND FREE RADICAL REACTIONS IN RADIATION CHEMISTRY
T. F. Williams - Department of Chemistry

Radiation effects in liquids and solids, chemical reactions of highly reactive intermediates (ions and free radicals) generated by the passage of radiation. Paramagnetic intermediates possessing an unpaired electron, detection by electron spin resonance (ESR) spectroscopy; negative ions of fluorocarbons and other molecules formed by electron attachment to the parent molecule. Demonstration of electron attachment to many so-called saturated molecules; hypervalent radical ions, ionization and electron attachment processes as primary mechanisms of radiation damage. Ions discovered include (MeO)₃P-P(OMe)₃⁺, Me₂Se-SeM₂⁺, F₃NO⁻, c-C₃F₆⁻, c-C₄F₈⁻, c-C₅F₁₀⁻, CF₃X⁻ (X = Cl, Br, I).

UNIVERSITY OF TEXAS

304. PHOTOELECTROCHEMISTRY AND MOLECULAR STORAGE OF SOLAR ENERGY
M. A. Fox - Department of Chemistry

Organic photoelectrochemistry. Identification of mechanisms in cells where an organic species photoemits electrons into an electrode and then accepts electrons from a second electrode. Measurement of potentials and quantum efficiencies. Study of photoejection mechanisms using flash photolysis and fast spectroscopic techniques. Mechanisms of subsequent reactions. Cyclooctatetraene and derivatives in various solvents. Micellar systems will be introduced to compare mechanisms and efficiencies of photoejection in these environments. In systems having low photoejection efficiencies, valence isomerizations will be studied mechanistically to determine optimum conditions for storing light energy chemically and releasing it as heat.
Reactions of high energy radioactive multivalent isotopes such as $^{31}\text{Si}$, $^{32}\text{P}$, and $^{11}\text{C}$ formed by nuclear transformations; abstraction, addition and insertion reactions of these hot atoms and their derived radicals in organic as well as inorganic systems; major controlling factors as well as the reaction mechanism for the hydrogen and halogen-abstraction processes; relative efficiencies of various olefin addition reactions involving $^{31}\text{Si}$ or $^{32}\text{P}$, or their derived species, such as $^{31}\text{SiH}_2$, $^{31}\text{SiF}_2$ and $^{32}\text{PH}$. Irradiation either with a nuclear reactor or with a cyclotron, analysis by radio-gas chromatography.

This research is to demonstrate the value of polymeric reagents as mechanistic probes in heterogeneous catalysis. Catalytically active metal complexes bound to polymers are such polymeric reagents which are alternatives to conventional homogeneous catalysts. This research is concerned with the development of specific functionalized polymers as catalysts and the demonstration of the use of immobilized, phase-separated trapping agents to identify intermediates in heterogeneous processes. Such catalysts possess the activity and selectivity of homogeneous catalysts and the experimental simplicity of heterogeneous catalysts.

Determination of the surface complexes and intermediates responsible for the reaction of either carbon monoxide or carbon dioxide with hydrogen to form methane (the methanation reaction), active metal catalysts supported on surfaces of silica or zeolites, kinetic and spectroscopic data and model compounds employed to establish the nature of the important intermediates in the catalytic reactions. Study of the intermediates which are present on active ruthenium metal catalysts, selectivity of bimetallic clusters involving ruthenium, possibility of intermediates existing in the gas phase after being formed on the surface and the reactivity of model intermediates such as ruthenium carbonyl hydrides. Determination of the ruthenium metal in zeolites for the methanation reaction.
TEXAS SOUTHERN UNIVERSITY

308. SOLVENT EXTRACTION $28,580 02-02
STUDIES USING HIGH-
MOLECULAR-WEIGHT AMINES
C. McDonald - Chemistry
Department

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

309. DYNAMICS AND MECHANISMS $46,000 01-01
OF HOT CHEMISTRY STIMULATED
BY RECOIL METHODS
L. D. Spicer - Chemistry Department

Reaction kinetics, atomic and molecular collision dynamics, and energy transfer in very high temperature systems, characterization of intramolecular and intermolecular flow of internal energy in hot molecules generated by recoil reactions. Decomposition kinetics of excited cyclobutane-t in the presence of selected bath gases, to explore intermolecular vibrational energy transfer from high levels of excitation and quantitatively characterize the kinetically controlled chemical activation technique. Chemical activation by recoil stimulated hot reaction at selected sites in haloalkyl cyclopropanes to study intramolecular energy transfer along the carbon backbone of alkane molecules, and to identify the time required for energy randomization in vibrationally excited hydrocarbons. Reactive deuterium isotope effects in molecular collisions at high relative, translational energies to elucidate dynamical factors in high energy collisions.
UNIVERSITIES -121-

VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

310. REACTIONS OF CHARGED AND NEUTRAL RECOIL PARTICLES FOLLOWING NUCLEAR TRANSFORMATIONS
H. J. Ache - Chemistry Department

Kinetics of chemical reactions (in the gas, liquid and solid phase) occurring with nuclear-reaction-produced species not in thermal equilibrium with its surroundings. Reactions of nuclear-reaction-produced nuclides in solution, effect of the physical properties, such as dielectric constants, etc. of the solvent on the reaction pathways. Use of chemical effects of nuclear transformations to devise simple and direct methods to incorporate short-lived radio-nuclides into organic or biomolecules to prepare radiopharmaceuticals for diagnostic application in nuclear medicine. Reactions of "hot" tritium atoms generated in nuclear reactions with various reactor wall materials.

WASHINGTON UNIVERSITY

311. REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS
P. P. Gaspar - Department of Chemistry

The finding and understanding of new high energy reactions of silicon and germanium atoms and of molecules containing these elements are the goals of this study. Silicon and germanium resemble carbon in being able to form complex and useful molecules.

In this project high energy silicon and germanium atoms are generated and allowed to react with simple organic and inorganic compounds. The reactions are chosen so that the structures of the products help to reveal the details of the reaction sequence by which the free silicon and germanium atoms become incorporated in stable molecules. On their way toward becoming stable molecules silicon and germanium atoms are converted into short-lived species with one, two, and three bonds to the silicon and germanium atoms. These intermediates are very reactive and a major goal of this research is to determine the structures of these intermediates and to learn how the form and the amount of the energy carried by these intermediates influence their reactions.

In these studies silicon and germanium atoms are produced by nuclear recoil and by thermal evaporation. Divalent silicon and germanium radicals are produced by low pressure pyrolysis and by photolysis.
WAYNE STATE UNIVERSITY

312. RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES
L. Kevan - Department of Chemistry

$90,000 01-01

Reactive reaction intermediates in disordered systems; spin-lattice energy relaxation mechanisms of radiation-produced radicals in disordered systems studied by pulsed electron spin resonance; matrix dipolar interactions of trapped radicals studied by electron spin echo spectrometry; magnetic energy transfer and forbidden spin transitions by electron-electron double resonance; electron solvation in mixed solvents by laser photolysis; transport properties of electrons in condensed phase alkanes by conductivity and mobility methods; trapped radicals and ions produced by sub 4 K radiolysis by electron spin resonance and optical methods. Trapped electrons in alkane glasses; trapped radicals in glasses; electron-electron radical-radical correlation distances; electron localization in alkanes has been developed.

313. ELECTRONIC RELAXATION PROCESSES IN POLYATOMIC MOLECULES
E. C. Lim - Department of Chemistry

$48,000 01-02

Radiationless transitions in polyatomic molecules; conversion of electronic energy into vibrational (heat) energy and factors which govern the efficiency of these processes. Excitation by light and heat energy detection directly by opto-acoustic signals or, indirectly, via molecular luminescence.

COLLEGE OF WILLIAM AND MARY

314. THEORY OF PLASMA WAVES IN THE EARTH'S BOW SHOCK
S. P. Gary - Physics Department

$22,700 01-03

Theoretical investigation of possible plasma instabilities in the earth's bow shock; solution of the complete electromagnetic, Vlasov, linear dispersion relation for conditions appropriate to perpendicular shocks, dominant instabilities, construction of appropriate nonlinear theories to determine saturation mechanisms and turbulent scattering frequencies. Structure of the earth's bow shock and how it heats the solar wind plasma. Dispersion relation for the case of unmagnetized ions and magnetized electrons undergoing an $\vec{E} \times \vec{B}$ drift.
315. STUDIES IN HOT ATOM CHEMISTRY AND RADIATION CHEMISTRY
J. E. Willard - Department of Chemistry

Nature and reactions of molecular fragments produced in organic solids by energy absorbed in the form of radiation, gamma rays, high speed electrons and ultraviolet light. Primary decomposition products are electrons, positive ions and free radicals. Solids at low temperatures (e.g., 4 K to 77 K); prolonged observation of fragments because diffusion is slowed and energy required for normal reactions is not available. Mechanisms of charge stabilization in relatively non-polar matrices and of its neutralization and reaction with additives; unexpected effects of substituting deuterated matrix molecules for protiated molecules; distinctive properties of radicals produced in close proximity; production of radicals in the solid state by mercury photosensitization; physical and chemical properties of the organic solid state. Evidence from visible, infrared, ultraviolet and electron spin resonance spectra and from luminescence, thermal effects and electrical conductivity.

316. INELASTIC MOLECULAR COLLISIONS-
APPLICATIONS OF THEORETICAL METHODS TO PROBLEMS IN RELAXATION PHENOMENA AND LASER OPERATION
R. W. Conn - Nuclear Engineering Department

Studies of inelastic molecular collisions: development and implementation of new theoretical methods capable of handling realistic collision problems, mathematical methods and Hamiltonian-type techniques, vibrational relaxation of hydrogen fluoride (HF) and carbon monoxide (CO), modeling of HF lasing under various experimental conditions.

317. METAL CATALYZED HYDROGENATION OF CARBON MONOXIDE TO HYDROCARBONS
C. P. Casey - Department of Chemistry

This research involves the synthesis of new metal formyl complexes, a study of their thermodynamic and kinetic stability, and investigations of the further reduction of these complexes. Also of interest is the termination of hydrocarbon chain growth from a metal catalyst which is believed to involve the hydrogenation of a metal-carbene complex. This research relates to the eventual design of homogeneous catalysts for the reduction of carbon monoxide.
WORCESTER POLYTECHNIC INSTITUTE

318. THE GAS PHASE RADIOLYSIS AND VACUUM ULTRAVIOLET PHOTOLYSIS OF HETEROCYCLIC ORGANIC COMPOUNDS

A. A. Scala - Chemistry Department

Interaction between high energy radiation and heterocyclic organic compounds; gas phase gamma-radiolysis and vacuum ultraviolet photolysis; primary and secondary modes of decomposition of complex organic molecules, factors which affect the reactions in these systems. Concern with ions as well as neutral excited molecules, deduce information concerning energy distribution in the decomposing molecules. Quasi-equilibrium situations, thermodynamic factors such as bond energies significant in determining reaction channels.

WRIGHT STATE UNIVERSITY

319. THE DIRECT DETERMINATION OF ATOM AND RADICAL CONCENTRATIONS IN THERMAL REACTIONS OF HYDROCARBONS AND OTHER GASES

G. B. Skinner - Department of Chemistry

A program to measure concentrations of species such as H, O, OH and CH₃ in shock-heated mixtures of smaller hydrocarbons diluted with argon, sometimes in the presence of oxygen; atomic (or molecular) absorption spectroscopy; high temperature reactions of several hydrocarbons.

YALE UNIVERSITY

320. RESEARCH ON HIGH-ENERGY CHEMICAL REACTIONS

R. J. Cross - Department of Chemistry

Chemical reaction rate dependence on the energy of the colliding molecules; one reacting species in a beam at a known and variable energy; amount of product formed measured as a function of beam energy. Theory to calculate the rate of energy loss of a fast atom as it collides with slow molecules.
321. ENERGIES OF ORGANIC COMPOUNDS
K. B. Wiberg - Department of Chemistry

Experimental studies on the energies of molecules and development of methods for estimating the energies of molecules; development of automated systems for collecting calorimetric data; determination of the appropriate interaction parameters for the molecular mechanics method for estimating energies; ab initio molecular orbital calculations.
SECTION C

Summary of
Funding Levels
During the fiscal year ending September 30, 1977, the Chemical Sciences total support level amounted to about $33.6 million in operating funds and $2.6 million in equipment funds. The equipment funds are expended primarily at the Government-owned Laboratories and are not shown in this report. Equipment funds for the University and Corporate projects are included in the total contract dollars, being part of the operating budget. The following analysis of costs is concerned only with operating funds.

1. By Region of the Country:

<table>
<thead>
<tr>
<th>Region</th>
<th>Contract Research (%)</th>
<th>Total Program (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Northeast</td>
<td>35.7</td>
<td>25.8</td>
</tr>
<tr>
<td>(b) South</td>
<td>9.0</td>
<td>17.8</td>
</tr>
<tr>
<td>(Ala., Fla., Ga., Miss., S. C., Tenn., Va., W.Va.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Midwest</td>
<td>29.3</td>
<td>35.0</td>
</tr>
<tr>
<td>(Ill., Ind., Iowa, Kans., Mich., Minn., Mo., Nebr., Ohio, Wis.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d) West</td>
<td>26.0</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

2. By Laboratory and University Programs:

<table>
<thead>
<tr>
<th>Program</th>
<th>Total Program (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) University Program</td>
<td>38.4</td>
</tr>
<tr>
<td>where graduate students are involved in</td>
<td></td>
</tr>
<tr>
<td>research to a large extent, e.g., Ames</td>
<td></td>
</tr>
<tr>
<td>Laboratory, Lawrence Berkeley Laboratory,</td>
<td></td>
</tr>
<tr>
<td>Notre Dame University (Radiation Laboratory)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.4</td>
</tr>
<tr>
<td>(b) Laboratory Program</td>
<td>59.6</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Other</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>
3. By Laboratory:

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Total Program (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ames Laboratory</td>
<td>5.9</td>
</tr>
<tr>
<td>Argonne National Laboratory</td>
<td>17.0</td>
</tr>
<tr>
<td>Atomics International</td>
<td>0.3</td>
</tr>
<tr>
<td>Bartlesville Energy Research Center</td>
<td>0.2</td>
</tr>
<tr>
<td>Brookhaven National Laboratory</td>
<td>18.6</td>
</tr>
<tr>
<td>Lawrence Berkeley Laboratory</td>
<td>10.0</td>
</tr>
<tr>
<td>Lawrence Livermore Laboratory</td>
<td>0.7</td>
</tr>
<tr>
<td>Los Alamos Scientific Laboratory</td>
<td>1.6</td>
</tr>
<tr>
<td>Morgantown Energy Research Center</td>
<td>0.2</td>
</tr>
<tr>
<td>Mound Laboratory</td>
<td>1.9</td>
</tr>
<tr>
<td>Notre Dame University (Radiation Laboratory)</td>
<td>4.4</td>
</tr>
<tr>
<td>Oak Ridge National Laboratory</td>
<td>15.7</td>
</tr>
<tr>
<td>Pacific Northwest Laboratory</td>
<td>2.8</td>
</tr>
<tr>
<td>Sandia Laboratory</td>
<td>0.6</td>
</tr>
<tr>
<td>Contract Research</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>

4. By Budget Number/Title

<table>
<thead>
<tr>
<th>Budget Number/Title</th>
<th>Contract Research (%)</th>
<th>Total Program (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-01 Radiation Sciences</td>
<td>35.5</td>
<td>28.5</td>
</tr>
<tr>
<td>01-02 Chemical Physics</td>
<td>15.9</td>
<td>20.5</td>
</tr>
<tr>
<td>01-03 Atomic Physics</td>
<td>19.2</td>
<td>10.8</td>
</tr>
<tr>
<td>02-01 Chemical Energy</td>
<td>14.5</td>
<td>19.9</td>
</tr>
<tr>
<td>02-02 Separations</td>
<td>10.6</td>
<td>10.6</td>
</tr>
<tr>
<td>02-03 Analysis</td>
<td>2.8</td>
<td>8.9</td>
</tr>
<tr>
<td>02-04 Engineering Sciences</td>
<td>1.5</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>
SECTION D

Index of Investigators

The index refers to project numbers in Sections A and B.
Abell, G. C., 111
Ache, H. J., 310
Agron, P. A., 139
Appelman, E. H., 40, 42, 45
Aris, R., 271
Arnold, W. D., 141
Ashurst, W. T., 167
Avona, V. L., 114

Baes, C. F., 137
Bamberger, C. E., 136
Barnes, R. M., 262
Barnett, C. F., 133
Bartlett, N., 97
Bassham, J., 90
Bayfield, J. E., 294
Beauchamp, J., 235
Begovich, J. M., 147
Bell, A. T., 94
Bell, J. T., 142
Benjamin, B. M., 140
Bergbreiter, D. E., 306
Berkowitz, J., 34
Bernstein, H., 56
Berry, H. G., 38
Berry, W. B., 125
Beuhler, R., 58
Bielski, B. H. J., 50
Bigeleisen, J., 300
Bowman, R. C., 111
Brauer, F. P., 163, 166
Brenner, D., 54
Brink, G. O., 283
Broida, H. P., 230
Bryant, H. C., 280
Brynestad, J., 144
Burkhart, R. D., 279
Burwell, R. L., 285
Butt, J. B., 285

Cafasso, F. A., 47
Callaway, J., 258
Canada, D. C., 154
Canon, R. M., 147
Carlson, T. A., 132

Carr, R. W., Jr., 269, 271
Carruthers, J. A., 272
Casey, C. P., 317
Cattolica, R. J., 167
Chanin, L. M., 272
Chen, T. C. S., 212
Cheung, J. T. K., 129
Childs, W. C., 36
Chiu, L.-Y. C., 248
Christie, W. H., 153
Christoffersen, R. E., 255
Clardy, J., 13
Clarke, R. H., 215
Clem, R., 100
Clinton, S. D., 147, 148
Cohen, J. B., 285
Cohen, S. G., 219
Coleman, C. F., 149
Collins, C. J., 140
Conn, R. W., 316
Connick, R. E., 93
Corliss, L., 60
Cox, J. L., 157
Cram, D. J., 227
Crandall, D. H., 133
Crawford, O. H., 131
Creutz, C., 53
Cross, R. J., 320
Crosswhite, H. M., 30

Dale, J. M., 155
Dalgarno, A., 247
Davis, M. W., Jr., 301
Demmitt, T. F., 158
DeWitt, R., 114
Dittner, P. F., 129
Dodson, R. W., 50
Dole, M., 214
Donohue, D. L., 152
Dorfman, L. M., 287
Douslin, D. R., 49
Dworkin, A. S., 144
Dye, J. L., 267
INVESTIGATORS

Eby, R. E., 153
Egan, B. Z., 146
Egan, J. J., 73
Ehrenson, S., 57
Eland, J. H. D., 34
El-Sayed, M. A., 226
Erickson, N. E., 210
Espenson, J., 8, 10
Evans, W. J., 237

Fajer, J., 63
Fano, U., 236
Farr, J. D., 108
Fasse1, V., 15
Feder, H. M., 47
Feldberg, S., 64
Feldman, C., 151
Feldman, W. C., 106
Ferraro, J., 33
Fessenden, R. W., 122
Filipescu, N., 243
Finston, H. L., 281
Firestone, R. F., 286
Fischer, C. F., 291
Fisher, P. W., 148
Fontijn, A., 201
Ford, P. C., 231
Fowler, J., 51
Fox, M. A., 304
Franklin, J. C., 154
Franz, J. A., 159
Freiser, H., 213
Friedman, A. M., 46
Friedman, L., 58
Fritz, J., 16
Fulcher, E. L., 139
Funabashi, K. P., 116

Gaines, G. L., 204
Gallup, G., 278
Garrison, W. M., 79
Garvin, D., 208
Gary, S. P., 314
Gaspar, P. P., 311
Gemmell, D. S., 39
Gentry, W. R., 270
Gerstein, B., 12
Giauque, R., 100

Gilpatrick, L. O., 144
Goles, R. W., 162
Good, W. D., 49
Goodman, L. S., 36
Gordon, G. E., 261
Gordon, R. J., 251
Gordon, R. L., 165
Gordon, S., 24, 25
Greene, E. F., 220
Grens, E. A., 98
Grover, J., 59

Hagaman, E. W., 140
Hambright, P., 250
Hamill, W. H., 125
Hammond, G. S., 233
Hampson, R. F., 208
Hanrahan, R. J., 241
Hanson, R. K., 302
Harbottle, G., 51, 71
Hardesty, D. R., 167
Harris, C. B., 80
Harris, L. A., 205
Hastings, J., 60
Headley, L. C., 110
Henry, R. J. W., 258
Hildenbrand, D. L., 206
Hill, F. B., 75
Hill, R. A., 167
Hillman, M., 61
Hochanadel, C. J., 126
Hoffman, D., 4
Hoffman, M. Z., 216
Holmes, H. F., 137
Holroyd, R. A., 50
Horowitz, E. P., 43
Hudis, J., 69
Hulett, L. D., 155
Hurst, F. J., 141

Ishida, T., 282
Ivey, J. L., 111

Jackson, W. M., 249
Jepson, B. E., 112
Johnsen, R. H., 242
Johnson, J. S., 143
INVESTIGATORS

Johnston, H. S., 78
Jolly, W. L., 95
Jones, G., 217
Jones, K. W., 67, 77
Jones, L., 105

Kaminsky, M., 35
Kaplan, L., 25
Karapinka, G. L., 109
Katz, J. J., 26, 28, 29
Katzer, J. R., 239
Kaufman, J. J., 254
Kaye, J. H., 161
Kee, R. J., 167
Kelley, J. M., 164
Kelley, R. D., 210
Kemme, J. E., 104
Kessler, K. G., 209
Kestner, N. R., 257
Kevan, L., 312
King, A. D., 244
King, R. B., 244
Kispert, L. D., 212
Klatt, L., 155
Klemm, R., 66
Kleppner, D., 265
Klinglen, T. J., 273
Knaurer, J. B., 150
Koetzle, T., 56
Koski, W. S., 254
Kozak, J. J., 117
Kraner, H. W., 77
Krause, H. F., 129
Krikorian, O., 102
Kruger, C. H., 302
Kubas, G., 107
Kuppermann, A., 234

Lagergren, C. R., 165
Lambrecht, R. M., 51
Lampe, F. W., 290
Lane, N. F., 299
Law, C. K., 284
Lawson, W. F., 110
Lee, E. K. C., 222
Lee, M. H., 246
Lee, S. H., 49
Lee, Y. T., 86

Leventhal, J. J., 274
Li, C. T., 160
Lichtin, N. N., 216
Lietzke, M. H., 137
Lim, E. C., 313
Linschitz, H., 218
Lipsky, S., 268
Livingston, R., 130
Lloyd, M. H., 150
Lonsdale, H. K., 203
Love, C. M., 111
Lunsford, J. H., 307

MacDonald, J. R., 256
Macek, J. H., 278
Mackay, R. A., 240
Mackenzie, D. R., 74
Madey, T. E., 210
Maggiora, G. M., 255
Mahan, B. H., 83
Mailen, J. C., 145
Malm, J. G., 40
Marrus, R., 89
Marshall, W. L., 137
Martin, D., 2, 11
Martin, R. N., 229
Matheson, M. S., 21, 23
McDonald, C., 308
McDowell, W. J., 149
McLean, W. J., 238
McMullan, R., 56
Meisels, G. G., 276
Michaels, E. D., 112
Miller, J. A., 167
Miller, J. R., 22
Miller, P. D., 134
Miller, W. H., 84
Mitchell, R. E., 167
Moak, C. D., 134
Molton, P. M., 158, 159
Morgan, H. W., 135
Morrey, J. R., 156
Mozumder, A., 116
Muckerman, J., 57
Mudge, L. K., 160
Myers, A. L., 289
Myers, R. J., 81
INVESTIGATORS

Neta, P., 123
Netzel, T., 55
Newman, J. S., 96
Newman, L., 76
Newton, M., 57
Ng, C., 7
Nicol, M. F., 225
Norcross, D. W., 211
Norris, J. R., 27
Novakov, T., 92

Oskam, H. J., 272
Otvos, J., 90
Overbury, S. H., 128

Packer, L., 91
Patterson, L. K., 123
Pearlstein, R. M., 127
Perlman, M. L., 69
Perlmutter, D. D., 289
Perlow, G., 37
Perone, S. P., 297
Pitzer, K. S., 82
Poe, R. T., 228
Powell, J., 14
Pratt, D. W., 293

Raaen, V. F., 140
Rabitz, H., 295
Rack, E. P., 275
Rahn, L. A., 167
Rainey, W. T., 154
Regen, S. L., 259
Reilly, J. J., 72
Richard, P., 256
Richardson, D. M., 136
Rinker, R. G., 232
Robben, F., 101
Robertson, D. M., 164
Robinson, D. W., 253
Rodgers, B. R., 147
Rogers, L. B., 245
Rogers, M. T., 266
Root, J. W., 221
Ross, A., 121
Ross, J., 264
Routh, J. W., 103

Rowland, F. S., 223
Ruedenberg, K., 6
Rutherford, W. M., 112

Samson, J. A. R., 277
Sauer, M. C., 22
Sayre, E. V., 71
Scala, A. A., 318
Schaefer, H. F., 87
Schreiner, F., 42
Schuler, R. H., 118
Schwartz, M. E., 117
Schwarz, H. A., 50
Seltzer, S., 68
Setchell, R. E., 167
Shaw, R. W., 155
Sheng, S. J., 115
Shirley, D. A., 85
Shor, A. J., 143
Shugart, H. A., 88
Silverman, J., 260
Simmons, W. H., 110
Skinner, G. B., 319
Small, G., 1
Smith, D. H., 138, 152
Smith, G. P., 144
Smith, J. R., 167
Somorjai, G. A., 94
Spaulding, L., 65
Spedding, F., 9
Spicer, L. D., 309
Starace, A. F., 277
Stein, L., 40
Stelzner, R. W., 151, 153
Stevens, C. M., 45
Stoenner, R. W., 71
Strain, J. E., 151
Strehlow, R. A., 139
Struve, W., 3
Studier, M. H., 41, 44
Stwalley, W. C., 252
Sutherland, J. W., 62
Sutin, N., 53
Svec, H., 5, 17
Sworski, T. J., 126
Tang, Y.-N., 305
Tanner, R., 76
Taylor, W. L., 113
Thomas, J. K., 119
Thomas, R., 56
Thomson, D. B., 105
Tingey, G. L., 156
Toth, L. M., 142
Treat, R. P., 110
Trozzolo, A. M., 120
Tsao, G. T., 298
Turkevich, J., 296

Ulrichson, D., 11

Valenty, S. J., 204
Vannice, M. A., 292
Vermeulen, T., 98
Victor, G., 247
Voigt, A., 18

Wahl, A. C., 32
Walker, R. L., 152
Walters, G. K., 299
Walters, W. B., 261
Wentorf, R. H., Jr., 205
Weston, R. E., 52, 70
Wexler, S., 31
White, D., 288
Wiberg, K. B., 321
Wiese, W. L., 209
Wilke, C. R., 99
Willard, J. E., 315
Williams, E. T., 281
Williams, T. F., 303
Wilson, R. H., 205
Winicur, D. H., 124
Wise, H., 207
Wiswall, R., 72
Wolf, A. P., 51
Wolfsberg, M., 224
Wrighton, M. S., 263

Yang, R. T., 74
Yates, J. T., 210
Yeung, E., 19, 20
Yosim, S. J., 48
SECTION E

INDEX OF PROJECTS

GROUPED BY

PROGRAMMATIC AREA
01-01 RADIATION SCIENCES

Research involving the chemical reactions and species formed as the result of the introduction of radiation or high energy particles into chemical systems, including the chemical effects of radioactive decay and especially solar-induced photochemistry.


01-02 CHEMICAL PHYSICS

Basic studies of gas phase ion and molecule interactions; optical, magnetic, particle, and mass spectroscopy as they relate to chemical reactivity; the determination of molecular structure and its relationship to molecular properties; and theoretical studies including quantum theory, kinetic theory, and statistical thermodynamics and their use for the prediction of chemical and physical properties.

4, 5, 6, 7, 30, 31, 32, 33, 56, 57, 58, 59, 60, 64, 65, 66, 80, 81, 82, 83, 84, 85, 86, 87, 92, 129, 130, 131, 167, 201, 208, 220, 222, 225, 226, 229, 230, 238, 248, 249, 251, 264, 267, 270, 274, 283, 284, 288, 293, 295, 302, 313, 316, 319, 320

01-03 ATOMIC PHYSICS

Research activities primarily related to the physics of matter in the gaseous, ionic and plasma states: spectroscopy, collision phenomena, atomic structure and dynamics.

02-01 CHEMICAL ENERGY

Research in thermodynamics, solution kinetics, electrochemistry, inorganic chemistry, the study of heterogeneous and homogeneous catalysts, energy conversion processes, and basics of the production and storage of chemical fuels such as liquefied coal and hydrogen.


02-02 SEPARATIONS RESEARCH

Research on the effects of isotopic substitution on the physical and chemical properties of atoms and molecules which can be used as either theoretical or experimental tools to effect isotope separation, as well as research on the separation methods themselves; research on methods of separating and purifying chemical species and research on the separation of materials in different physical states.

14, 43, 70, 75, 110, 112, 113, 114, 141, 142, 143, 147, 148, 149, 150, 202, 203, 213, 224, 227, 245, 246, 271, 272, 282, 300, 301, 308

02-03 ANALYSIS

Basic and developmental studies in laboratory analytical techniques and methods.

15, 16, 17, 18, 19, 20, 44, 45, 46, 71, 76, 77, 100, 151, 152, 153, 154, 155, 161, 162, 163, 164, 165, 166, 261, 262, 281

02-04 CHEMICAL ENGINEERING SCIENCES

Experimental and theoretical research involving mass, heat and momentum transport, and related chemical rate processes; engineering modeling, process control and engineering and chemical thermodynamic studies related to energy technologies.

101, 103, 160, 232, 289
Available from:

National Technical Information Service (NTIS)
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price:
Printed Copy: $ 8.00
Microfiche: $ 3.00