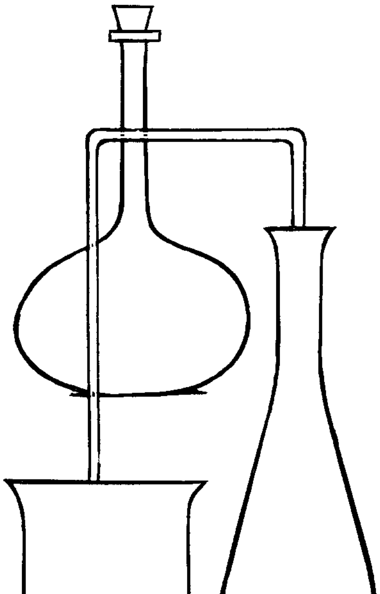
TID-4005(Pt. 2b)

SUMMARIES OF THE USAEC BASIC RESEARCH PROGRAM IN CHEMISTRY (ON SITE)

August 1964



Division of Research, AEC

UNITED STATES ATOMIC ENERGY COMMISSION
Division of Technical Information

Printed in USA. Price $7.90. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Va.

USAEC Division of Technical Information Extension, Oak Ridge, Tennessee

TID-4005(Pt. 2b)
CHEMISTRY
(TID-4500, 33rd. Ed.)

SUMMARIES OF THE USAEC BASIC RESEARCH PROGRAM IN CHEMISTRY (On Site)

Division of Research, AEC

Indexes prepared by
Division of Technical Information Extension

August 1964

UNITED STATES ATOMIC ENERGY COMMISSION
Division of Technical Information

FOREWORD

The Atomic Energy Act directs the Atomic Energy Commission to support and foster research in the field of atomic energy. The Division of Research of the Atomic Energy Commission is responsible for accomplishing this objective in the physical sciences. Research is supported at the AEC National Laboratories, at other Government Laboratories, at universities, at research institutes and foundations and at industrial laboratories.

The Chemistry Program is administratively divided into the "on-site" and the "off-site" programs. The "on-site" program is carried out at the AEC Laboratories and other Government-owned facilities. The "off-site" program is carried out elsewhere and consists primarily of research projects performed through contracts with educational institutions.

This document summarizes the objectives and current status of the individual research projects supported by the Office of Chemistry Programs of the Division of Research under its "on-site" program. Projects supported at the National Bureau of Standards are also included.

It is the purpose of this document to inform the scientific community of the current researches being supported.

The summaries have been organized and numbered according to the place where work is carried out. There is also a comprehensive subject index included to permit detailed search for information by subject. Each summary includes the name of the Laboratory at which the work is carried out, the Department or Division, the principal investigator or investigators, and the date on which the summary was received.

All of the research presented in this document is unclassified and investigators are encouraged to report their results in the open literature at the earliest opportunity for wide dissemination of the information. The interested reader is referred to Nuclear Science Abstracts or to Chemical Abstracts as sources of information concerning publications resulting from the work summarized in this document.

Inquiries or comments concerning the researches described should be directed to:

Dr. A. R. Van Dyken
Assistant Director of Research
for Chemistry Programs
Division of Research, USAEC
Washington, D. C. 20545

TABLE OF CONTENTS

	Section
Ames Laboratory - Chemistry Division	1A
Ames Laboratory - Chemical Engineering Division	1B
Argonne National Laboratory - Chemistry Division	2A
Argonne National Laboratory - Chemical Engineering Division	2B
Brookhaven National Laboratory - Chemistry Department	3A
Brookhaven National Laboratory - Nuclear Engineering Department	3B
Hanford Atomic Products Operation - Hanford Laboratories	4
Lawrence Radiation Laboratory - Berkeley - Chemistry Division	5A
Lawrence Radiation Laboratory - Berkeley - Inorganic Materials Research Division	5B
National Bureau of Standards	6
University of Notre Dame - Radiation Laboratory	7
North American Aviation - Atomics International	7X
Oak Ridge National Laboratory - Chemistry Division	8A
Oak Ridge National Laboratory - Analytical Chemistry Division	8B
Oak Ridge National Laboratory - Reactor Chemistry Division	8C
Oak Ridge National Laboratory - Chemical Technology Division	8D

SECTION 1A

AMES LABORATORY - CHEMISTRY DIVISION

1A1 Electrometric Methods of Analysis

1A2 Investigation of Bifunctional Organophosphorous Compounds as Solvent Extractants

1A3 Chemistry of *vic* dioximes

1A4 Analytical Separations by Reversed-Phase Chromatography

1A5 Analytical Ion-Exchange Separations

1A6 Quantitative Determination of Interstitial Oxygen and Nitrogen Impurities in Metals

1A7 Analytical Emission Spectroscopy

1A8 Atomic and Molecular Absorption Spectra

1A9 Experimental Molecular Structure

1A10 Diffraction Techniques

1A11 Structural Chemistry

1A12 Interactions of Magnetic Species in Solids

1A13 Thermodynamic Properties and Related Properties of Aqueous Rare-Earth Chloride Solutions

1A14 Studies of Free Radical Reactions and Properties in Solution

1A15 Kinetics and Mechanisms of Inorganic Reactions

1A16 Surface Chemistry

1A17 Physico-Chemical Characterization of Inorganic Compounds by Mass Spectrometry

1A18 Instrumentation (Mass Spectrometry)

1A19 Physical and Chemical Properties of Reduced Metal Halides

1A20 Reaction of Metals with Their Molten Halides

SECTION 1A Continued

1A21	Phase Relation and Vaporization Reactions at High Temperatures
1A22	Chemical Effects in Nuclear Reactions
1A23	Physical Properties of Silver Halides
1A24	Chemistry of the Platinum Elements
1A25	Separation of Rare Earths by Ion Exchange
1A26	Separation of Light Isotopes
1A27	Determination of Stability Constants of Rare Earth Complex Species
1A28	High Purity Materials Studies Using Activation Analysis for Impurity Determination
1A29	Recoil Chemistry of Carbon-11

For further information on completed work, the reader is referred to the open scientific literature and to the Ames Laboratory Annual Summary Report for July 1962 through June 1963, IS-700, September 1963.

AMES LABORATORY
Chemistry Division

Charles V. Banks/Motomu Kasagi
George J. Kamin/Michael J. Fahsel

1/10/64

ELECTROMETRIC METHODS OF ANALYSIS

The sine-wave (A.C.) polarographic method has been found to give quite good results for the determination of small amounts of indium in the presence of large amounts of cadmium, lead, or tin. Niobium and zirconium can be determined in citric acid media with greater sensitivity than is obtainable with D.C. polarography. It is planned to apply the technique of sine-wave (A.C.) polarography to other cases where D.C. polarography is not suitable. The greater sensitivity of the A.C. method and the fact that much larger ratios of reducible species can be tolerated by the A.C. method than by the D.C. method makes the A.C. polarographic method a powerful analytical technique for the determination of trace impurities in "pure" metals.

The interaction of hydrogen ions with 1, 10-phenanthroline is not well understood. Experimental data on this system seem to suggest that poly-1, 10-phenanthroline-hydrogen ion species may exist in solution. It is planned to study this system in some detail to establish more clearly the species that are present in aqueous acid solution, and, if possible, measure the stability constants of these species.

A method for the coulometric titration of the alkaline earth cations following the separation of these ions by a reversed-phase chromatographic method was developed. The zones containing the individual cations were cut out and the cation eluted from the paper and titrated coulometrically with electrically generated EDTA. The EDTA was formed by the reduction of the EDTA-Hg complex at a mercury electrode. This technique is being extended to many other cations.

Publication

1. Dale and Banks, "Study of Metal-1, 10-Phenanthroline Complex Equilibria by Potentiometric Measurement," Inorg. Chem., 2, 591 (1963).

AMES LABORATORY Chemistry Division

C. V. Banks/J. W. O'Laughlin
J. W. Ferguson/J. E. Mrochek/R. Parker

1/10/64

INVESTIGATION OF BIFUNCTIONAL ORGANOPHOSPHORUS COMPOUNDS AS SOLVENT EXTRACTANTS

The separation of complex mixtures of elements is often necessary before the quantitative analysis of the individual components of the mixture can be made. The solvent extraction technique is one of the most powerful tools available to the analytical chemist for effecting such a preliminary separation. This research involves the synthesis and study of a new class of solvent extractants, bifunctional organophosphorus compounds and particularly bis(dialkylphosphinyl)alkanes.

Information on the nature of the adducts which these compounds form with various cations has been obtained by means of visible and infrared spectroscopic, conductometric, cryoscopic, liquid-liquid partition, and nuclear magnetic resonance techniques. It is anticipated that a better understanding of the nature of these adducts will result in the synthesis of even more powerful and selective extractants.

In addition to their usefulness in liquid-liquid extraction, some of these compounds are being studied as stationary phases in reversed-phase partition chromatography.

Publications

1. Mrochek, O'Laughlin, Sakurai, and Banks, "*gem* - Bis(di-substituted-phosphinyl)alkanes.II. Extraction of Uranium (VI) with Bis(di-*n*-hexylphosphinyl) Methane," *J. Inorg. Nucl. Chem.,* 25, 955 (1963).

2. Richard and Banks, "The Metalation of Methyl (disubstituted) Phosphine Oxides and Their Subsequent Reactions," J. Org. Chem., *28*, 123 (1963).

AMES LABORATORY

Chemistry Division

C. V. Banks/J. E. Caton, Jr.
N. A. Wilcox/ M. M. Barling

1/10/64

CHEMISTRY OF VIC-DIOXIMES

The vic-dioximes are widely known and used in analytical chemistry because of their striking selectivity as precipitants for certain metal ions. Results of x-ray crystal structure studies have greatly increased the understanding of the coordination chemistry of the vic-dioximes and have pointed the way to the synthesis of new and more versatile reagents. For example, the tert-butyl group in 4-tert-butyl-1, 2-cyclohexanedionedioxime sterically hinders crystal formation and results in an excellent extracting agent for nickel.

It is now known from x-ray diffraction studies that the hydrogen bonding in crystalling $Ni(DMG)_2$ and $Cu(DMG)_2$ are quite different. It is planned to study the rearrangement of these hydrogen bond systems, as the crystals are dissolved, by means of infrared, near infrared, and attenuated total reflectance spectra. This study should lead to a better understanding of the marked difference in the solubilities of these two compounds.

The solubility of the nickel-vic-dioxime complexes in non-coordinating solvents such as n-heptane would be expected to correlate rather well with the nickel-nickel distance in the crystalline state if the strength of this bond accounts for a large part of the crystal energy. It is planned to measure these solubilities and compare them with the known nickel-nickel distances. Such a study will contribute to our understanding of the selectivity of such organic analytical reagents.

Publication

1. Banks, "Vic-Dioximes as Analytical Reagents," Anal. Chem. 34, 131 (1962).

1A4

AMES LABORATORY Chemistry Division

James Fritz/Edward Hedrick 1/10/64

ANALYTICAL SEPARATIONS BY REVERSED-PHASE CHROMATOGRAPHY

The project includes the separation of both inorganic and organic substances by reversed-phase chromatography. A glass column is packed with an organic polymer impregnated with a solvent such as methyl isobutyl ketone, cyclohexane or benzene. Inorganic separations include the separation of molybdenum and iron from each other and from other elements. Organic separation of phenol mixtures and nitroaromatic amine mixtures have been realized, and many more are contemplated.

Publication

1. Fritz and Hedrick, "Separation of iron by reversed-phase chromatography," Anal. Chem. 34, 1411 (1962).

1A5

AMES LABORATORY Chemistry Division

J. Fritz/J. Abbink, Jr./R. Brown 1/10/64
L. Dahmer/R. Greene/H. Waki

ANALYTICAL ION-EXCHANGE SEPARATIONS

Separations are very important in many types of quantitative analysis. Work in progress includes the following approaches:

1. Separation of metal ions from a cation-exchange column by elution with aqueous-acetone solutions containing hydrochloric acid.

2. Cation-exchange separations by elution with dilute aqueous solutions of hydrofluoric acid.

3. Separation of Mo, W, Nb, and Ta from other metal ions by elution with dilute hydrogen peroxide.

4. Separation of rare earths from other metal ions by anion exchange using nitric acid in water-isopropyl alcohol solutions.

5. Separation of alkaline earth metals by anion-exchange using partly nonaqueous solutions.

Publication

1. Fritz and Garralda, "Cation-Exchange Separation of Bivalent Metal Ions from Rare Earths," Talanta 10, 91 (1963).

1A6

AMES LABORATORY Chemistry Division

Velmer A. Fassel/C. Matsumoto 1/10/64
W. Dallmann/R. Winge

QUANTITATIVE DETERMINATION OF INTERSTITIAL OXYGEN AND NITROGEN IMPURITIES IN METALS

The determination of the interstitial O and N impurity in metals and alloys at decreasingly lower concentration levels is a problem which is certain to remain live for some time. Particular attention is focused on critically evaluating and pin-pointing deficiencies in analytical methods now in use or under development, and on exploring fresh approaches. A new d.c. carbon-arc extraction, gas chromatographic technique for the rapid, simultaneous determination of O and N has been developed. Critical studies on the determination of oxygen in V and Th metals by the vacuum-fusion, inert gas fusion, and d-c carbon arc extraction methods have established the experimental conditions under which accurate data can be obtained. Continuing studies on the spectroscopic technique indicate that recent improvements in near-infrared sensitive detectors will make it possible to devise direct reading approaches. It is expected that further studies on the nature and kinetics of gas evolution reactions when metals are subjected to high temperature, high vacuum environmental conditions will lead to improvements in analytical methods based on vacuum extraction, fusion, or distillation processes.

Publications

1. Evens and Fassel, "Simultaneous Determination of Oxygen and Nitrogen in Steels by a DC Carbon Arc, Gas Chromatographic Technique," Anal. Chem., 35, 1444 (1963).

2. Fassel, Dallman, Skogerboe and Horrigan, "Comparative Study on the Determination of Oxygen in Vanadium Metal," Anal. Chem., 34, 1364 (1962).

AMES LABORATORY Chemistry Division

Velmer A. Fassel/Richard Kniseley/W.Grossmann 1/10/64

ANALYTICAL EMISSION SPECTROSCOPY

An effort is devoted to observing excitation processes that occur under environmental conditions far different from those normally employed by the analytical spectroscopist. Systematic explorations of interesting and useful spectra emitted in arc or spark discharges in supporting atmospheres other than air are laying the groundwork for the practical solution of difficult analytical problems; other types of excitation include induction-coupled plasmas and microwave discharge. These studies have led to a spectroscopic technique for determining the O content of niobium metal.[1]

Striking enhancements in the sensitivities of detection of atomic spectral lines emitted in flames have been realized by manipulating the chemical environment in simple flames. Atomic line spectra emitted in the interconal zone of premixed, fuel-rich oxyacetylene flames show detection sensitivities five orders of magnitude greater than the sensitivities observed in conventional turbulent flames. The simple atomic line spectra emitted by the rare earth elements in this interconal zone now provide the most convenient means for performing a complete analysis of rare earth mixtures. Observations on the atomic and molecular absorption spectra and emission spectra of the reaction zone, the interconal zone, and the outer cone of these flames should yield conclusive information concerning the formation of the interconal zone and the striking enhancement in atomic line spectra.

Publications

1. Evens and Fassel, "Emission Spectrometric Determination of Oxygen in Niobium Metal," Anal. Chem. 33, 1056 (1961).

2. Fassel, Curry and Kniseley, "Flame Spectra of the Rare Earth Elements," Spectrochim. Acta 18, 1127 (1962).

3. Kniseley, D'Silva and Fassel, "A sensitive, Premixed Oxy-acetylene Atomizer-Burner for Flame Emission and Absorption Spectrometry," Anal. Chem. 35, 910 (1963).

AMES LABORATORY Chemistry Division

V. A. Fassel/R. N. Kniseley 1/10/64
E. Conrad/R. Hirschmann/V. Mossotti

ATOMIC AND MOLECULAR ABSORPTION SPECTRA

Measurements on the $^{15}N/^{14}N$ isotope shift in vibrational frequencies provide data for identifying and characterizing vibrational modes involving appreciable nitrogen motion. A detailed study on benzamide revealed that the frequencies of the Amide I and Amide-II bands are inverted in the solid state, i.e., the Amide-II band lies at a higher frequency than the Amide-I band. Observations on the infrared spectra of substituted primary and secondary amides have clarified assignments on several characteristic vibrations and have yielded additional data on solid state intereactions in these compounds. A detailed vibrational analysis of alkyl thiocyanates has been completed. Inclusion of restricted rotation about both the C_α-C_β and C_α-S bonds, and associated rotational isomerism was required to satisfactorily account for the complex structure of the C_α-X stretching vibration.

The rare earth free-atom population in fuel-rich, oxy-acetylene flames fed with ethanol solutions of the perchlorate salts was found to be high enough to permit observation of the atomic absorption spectra of these elements. Among the more than 1000 lines observed are those of Eu, Dy, Ho, Gd, and Tb which have not been reported in the literature. The analytical applications of the stronger lines will be critically assessed.

Publication

1. Kniseley, Fassel and Farquar, "Infrared Spectra of Nitrogen-Containing Compounds I. Benzamide," Spectrochim. Acta 18, 1217 (1962).

1A9

AMES LABORATORY Chemistry Division

L. S. Bartell/H. B. Thompson 1/10/64

EXPERIMENTAL MOLECULAR STRUCTURE

The purpose of this program is to determine the structures and internal motions of gas molecules by electron diffraction techniques. Studies of stereochemistry, isotope effects, and internal rotation are being carried out to test current theories of valence and molecular force fields.

Deuterium isotope effects on bond lengths and amplitudes of vibration are under investigation in a series of first row hydrides. Novel conformational equilibria encountered in cyclopropane derivatives are being explored. Configurations with eclipsed bonds as well as the usual staggered bonds have been observed. The stereochemistry of phosphorus (V) derivatives is being studied to test the late Professor Rundle's theory of bonding. In addition, measurements of isotopic effects on molar volumes of hydrocarbon liquids are in progress.

The foregoing studies are useful in providing clues about intra- and inter-molecular forces.

1A10

AMES LABORATORY Chemistry Division

Donald R. Fitzwater/James E. Benson 1/10/64

DIFFRACTION TECHNIQUES

This program is primarily concerned with improving the experimental and computational techniques involved in X-ray and Neutron Diffraction studies of crystal structures. The increasing use of computers has had a tremendous impact on such techniques.

In conjunction with the Computer Services Group and with Dr. Robert M. Stewart, a general purpose, Shared Real Time Computer Control System has been designed and is being implemented. Among the experimental equipment to be controlled by this system will be Neutron and X-ray Diffractometers. Not only will larger volumes of high quality data be made available, but also new data gathering Algorithms will be developed.

Computer programs for the analysis and gathering of such data will be improved and expanded in power.

AMES LABORATORY Chemistry Division

D. R. Fitzwater/Yves P. Jeannin 1/10/64
David R. Russell/Aubrey J. Serewicz

STRUCTURAL CHEMISTRY

This program is designed to improve our understanding of the chemical bond. Compounds having interesting bonding and magnetic properties are studied in their crystalline form by X-Ray and neutron diffraction and by magnetic studies.

The abnormal deuterium isotope effect in 3,4-furandicarboxylic acid will be studied, and a structural study of dibenzoylmethane begun. Study of the cyclheptatrienyl-cyclopentadienyl manganese structure will be started. Work on ethylmagnesium bromide will be continued. Work on the triphenylalumimum structure will be started. Structural and magnetic measurements on copper complexes will continue, with a rebuilt magnetic susceptibility apparatus being utilized. Other crystal structures posing interesting structural, valence, or magnetic properties, to be determined as time permits are: $TeCl_4$ and $TeBr_4$, $C_5H_5FeMn(CO)_7$, ferrocen-$SnCl_4$ complex, IF_7, diphenylgermanium-2-butene complex, $KPtCl_3NH_3$, $HCoO_2$ and $DCoO_2$, $(C_6H_5)_2$ Si, $(NH_4)_2$ $SbBr_6$, $CsCuCl_3$, $KCrCl_3$, and $CuCl_2$-C_3H_7OH.

As neutron diffraction facilities become available they will be used in studies of strong hydrogen bonding and in studies of the magnetic properties of copper complexes.

Publications

1. Engebretson and Rundle, "The Molecular and Crystal Structures of π-Cyclopentadienyl π-Cycloheptatrienyl Vanadium," J. Am. Chem. Soc., 85, 481 (1963).

2. Willet, Dwiggens, Kruh and Rundle, "Crystal Structures of $KCuCl_3$ and NH_4CuCl_3," J. Chem. Phys., 38, 2429 (1963).

3. Rundle, "On the Probable Structures of XeF_4 and XeF_2," J. Am. Chem. Soc., 85, 112 (1963).

AMES LABORATORY Chemistry Division

B. C. Gerstein/F. J. Smentowski/Frank Jelinek 1/10/64

INTERACTIONS OF MAGNETIC SPECIES IN SOLIDS

The details of magnetic intereactions in both ordered (such as ferromagnetic) and non-ordered (paramagnetic) systems are still a matter of mystery, although a broad spectrum of magnetic phenomena may be qualitatively described by present theories incorporating approximate treatments of both types of systems. It is the purpose of the present work to investigate in detail magnetic interactions in both types of systems, ordered systems being characterized by rare earth metals, 3d transition group salts and stable free radicals, and paramagnetic systems by nine-hydrated rare earth ethyl sulfates, all systems presently under investigation in this group.

Investigations of the magnetically dilute rare earth salt systems via heat capacity and initial susceptibility measurements have complemented spectral studies in Professor Spedding's Spectroscopy Group, and are serving to critically test the crystalline field approximation as presently applied to 4f systems. It is hoped that such measurements will also provide information relevant to coupling of electronic and lattice excitations in such systems.

Studies of ordered systems, also by heat capacity and initial susceptibility measurements, complemented where possible by x-ray structure and epr work, are presently yielding effective exchange parameters for the rare earth metals, while work on the salts and radicals is just getting underway. Preliminary work on the radicals indicates that these may be ideal systems in which to test models of one- and two-dimensional ordering, and nearest-neighbor interactions only. It is hoped that such tests will be provided by completed measurements on radicals and non-stoichiometric oxides in the coming year.

Publication

1. Gerstein, Jennings, and Spedding, "Thermal and Magnetic Study of Crystal Field Splittings in Thulium Ethylsulfate," J. Chem. Phys. 37, 1496 (1962).

AMES LABORATORY Chemistry Division

F. H. Spedding/Herman Weber 1/10/64

THERMODYNAMIC PROPERTIES AND RELATED PROPERTIES OF AQUEOUS RARE-EARTH CHLORIDE SOLUTIONS

The availability of precise thermodynamic data and the related properties of aqueous rare-earth chlorides is of fundamental importance to a better understanding of ionic solutions. Since the rare-earths hydrolyze very slightly in aqueous solutions, have a charge of plus three, and a regularly decreasing ionic radii, they form an excellent series for the study of ionic solutions. These thermodynamic data are also essential to the study of aqueous rare-earth chemistry.

At the present time measurements are being carried out on partial molal volumes, partial molal expansibilities, activity coefficients, concentration cell potentials, viscosities, heats of dilution, and heat capacities of aqueous rare-earth chloride solutions. These measurements extend from very dilute concentrations up to the saturated solutions. Partial molal expansibilities, activity coefficients, concentration cell potentials, and viscosities are being measured as a function of temperature from 0.0°C to 80°C. The other measurements are being carried out at 25°C.

Emphasis is being given to measurements of concentrated solutions, since it is felt that these measurements will give valuable insight into the structure and nature of ionic solutions.

AMES LABORATORY Chemistry Division

Bernard C. Gerstein/Frank J. Smentowski 1/10/64

STUDIES OF FREE RADICAL REACTIONS AND PROPERTIES IN SOLUTION

The oxidation of organic mercaptans with inorganic oxidizing agents is a well known reaction, but the analogous reaction using organic agents is little known, and has been found to be a reaction of heretofore unrealized generality. We have found that organic aromatic mercaptans undergo electron transfer with organic electron acceptors to yield aromatic disulfides and the corresponding reduction products, and that radical anions having half lives of the order of hundreds of seconds are produced in the process. We have studied both the oxidation-reduction process for several mercaptan - electron acceptor pairs of agents and obtained information, via epr techniques, regarding spin density distributions in the radical anions. A typical example is the oxidation of nitroso benzene with the sodium salt of p-chloro benzene thiol, the reaction yielding the nitrosobenzene radical anion, and the corresponding disulfide dimer.

The immediate importance of the results of this study is the generalization of electron transfer reagents as oxidation reagents and the production of previously unknown radicals for study in solution and possibly as stable solid salts. It now appears that such salts, if they can be prepared, may supply some of the few examples where one observes linear antiferromagnetic ordering in the solid state with only nearest neighbor interactions. They will, therefore, serve as systems in which to critically test present theories regarding magnetic ordering.

Publication

1. Smentowski, "Electron - Transfer Reactions of Aromatic Thiolate Anions with Organic Oxidizing Agents," J. Am. Chem. Soc., 85, 3036 (1963).

AMES LABORATORY Chemistry Division

James H. Espenson/James P. Birk/Douglas E. Binau 1/10/64

KINETICS AND MECHANISMS OF INORGANIC REACTIONS

A study was made of the kinetics of the slow aquation (decomposition) of iodochromium(III) ion, CrI^{2+}. The low rate of this process also allows measurements of the kinetics of oxidation of bound iodide ion under conditions where appreciable free iodide ion is not formed; iodate ion, hydrogen peroxide, and iron(III) ion were studied as oxidizing agents.

Work is in progress on the following research problems: a kinetic study of the catalysis by chromium(VI) of aquation of $CrCl^{2+}$, to provide information on the rate and mechanism of formation and decomposition of unstable chromium(IV) and (V) in solution; kinetics and mechanisms for oxidation of iodide ion by chromium(VI) in acidic solution--further information on the roles of +4 and +5 oxidation states of chromium as reaction intermediates is sought here; kinetics and mechanisms for oxidation of vanadium(IV), and kinetics of formation and decomposition of complexes formed between hypophosphite ion and chromium(III), prior to a study of the kinetics of oxidation of hypophosphorous acid by chromium(VI).

Studies on the kinetics and mechanism of a number of additional inorganic reactions are planned, especially reactions of transition metal complexes in solution, and of oxidation-reduction reactions of metal ions. Particular attention in these investigations will be focused upon the roles as intermediates in these reactions of transition metal ions in unusual oxidation states, which will be characterized as completely as possible. In particular, studies are planned on the kinetics of oxidation reactions of lower oxidation states of transition metal ions, especially of vanadium, chromium, and iron complexes by reagents such as chromium(VI) and vanadium(V) and coordinated species of these as well. Underlying these studies is the desire to establish as completely as possible the mechanisms of these reactions with special attention to the question of how electron-transfer processes occur.

1A16

AMES LABORATORY Chemistry Division

Robert S. Hansen/Man Mohan Chaudhri/Peter Dawson 1/10/64

SURFACE CHEMISTRY

During the past year we have developed what we believe to be a powerful new approach to the study of viscoelastic properties of surface films through observation of propagation characteristics of capillary ripples. The approach includes both new theoretical and new experimental methods; during the next year we intend to apply it to systems with film-to-bulk transfer (soluble monolayers) and, hopefully, also to monolayers with reacting components.

We are further studying reactions on metal surfaces, particularly hydrocarbon decomposition reactions on representative Group VIII transition metals, using ultra-high vacuum field emission microscopy and flash filament desorption techniques, in an effort to establish the detailed kinetic mechanisms of these reactions.

An investigation of electrical double layer properties, particularly of the alteration of double layer capacitance by non-electrolyte adsorption and the usefulness of this alteration for the quantitative measurement of adsorption, is also in progress. During the next year we hope to perfect a method for measurement of capacitance at reversible interfaces by AC bridge techniques.

The limiting low-pressure Henry's Law constant in the gas adsorption isotherm provides, through its temperature dependence, information concerning the potential energy curve for gas-solid interaction. We are presently developing the use of gas adsorption chromatography for the determination of the potential function.

Publications

1. Mann and Hansen, "Propagation Characteristics of Capillary Ripples," J. Colloid Science 18, 757-71, 805-19 (1963).

2. Arthur and Hansen, "The Adsorption and Surface Reactions of Hydrocarbons on Clean Iridium," Annals of the New York Academy of Sciences 101, 756-65 (1963)

3. Hansen, Kelsh and Grantham, "The Inference of Adsorption from Differential Double Layer Capacitance Measurements. II. Dependence of Surface Charge Density of Organic Non-Electrolyte Surface Excess," J. Phys. Chem. 67, 2316-26 (1963).

4. Hansen and Murphy, "Low Temperature Limiting Behavior of Gas Imperfections due to Gas-Solid Interactions," J. Chem. Phys. 39, 1642-4 (1963).

AMES LABORATORY Chemistry Division

H. J. Svec/G. D. Flesch/G. Junk 1/10/64
J. Capellen/R. J. Conzemius

PHYSICO-CHEMICAL CHARACTERIZATION OF INORGANIC COMPOUNDS BY MASS SPECTROMETRY

Physico-chemical characterization of some volatile hydrides, halides, oxyhalides, chelating agents and chelates is difficult because of their instability, reactivity or inertness. The compounds are usually extremely toxic and/or corrosive. Mass spectrometric techniques can be successfully applied to physico-chemical problems where more conventional approaches are not possible. However, fundamental mass spectral data is non-existent for most of the compounds thus much of the work in this area is currently pioneering in nature. Methods and techniques for introducing and handling the compounds in the instrument have been developed and data processing has been improved to minimize or remove uncertainties and ambiguities in the results.

To date the scope of the work has included volatile Group IV and V hydrides, oxyhalides and halides of the first transition elements and inert elements, chelates and chelating agents. The results are fundamental to studies of absolute isotopic abundances of the elements and are of concern in isotope separations. During the coming year emphasis will be given compounds of Ti, fluorides of some noble metals, mixed dihydrides and copper and rare earth chelates.

Publications

1. Svec and Flesch, "Thermochemical Properties of XeF_2 and XeF_4 from Mass Spectra," Science, 142 954 (1963)

2. Svec and Junk, "Mass Spectra of α-Amino acids," J. Am. Chem. Soc., 85, 839 (1963).

3. Svec and Saalfeld, "Mass Spectra of the Monoelemental and Higher Hydrides of the Group IVB and VB Elements," Inorg. Chem. 2, 46, 51 (1963).

4. Svec and Flesch, "Absolute Abundance of Cr Isotopes in Primary and Secondary Minerals, " Geochim. et Cosmochim. Acta 20 300 (1960); Ibid. 26, 1351 (1962).

AMES LABORATORY Chemistry Division

H. J. Svec/G. D. Flesch/G. Junk 1/10/64
R. Conzemius/A. Anderson

INSTRUMENTATION (MASS SPECTROMETRY)

The mass spectrometry of unstable and/or corrosive inorganic compounds requires special handling techniques, heretofore unused in the field. Those compounds containing electronegative groups form positive and negative ions which introduce unique interpretive problems in order to obtain unique physico-chemical characterizations. The nature of the compounds requires that simultaneous measurements be made of the positive and negative ion currents. A model mass spectrometer which simultaneously detects positive and negative ions has been tested and a full scale instrument based on the pertinent design parameters of the model is being built. Unique construction problems arising from the basic principle of maintaining an electron gun at ground potential and accelerating the ions into high positive and negative fields have been solved. Emphasis at the same time is placed on safety and reliability of instrument operation. During the remainder of this year and the coming year the construction of this instrument will be completed along with pertinent sample handling systems. In addition a spark source mass spectrograph will be placed in operation and used for trace impurity analytical problems peculiar to the Ames Laboratory as well as research concerning matrix effects on the sensitivity of this instrument for element analysis.

Publications

1. Svec and Flesch, "Model of a Positive-negative Ion Mass Spectrometer," Rev. Sci. Inst. 34 897 (1963).

2. Svec and Conzemius, "Improvement of Ion Transmission in an Ion Source," J. Appl. Phys. 34 2486 (1963).

AMES LABORATORY Chemistry Division

J. D. Corbett 1/10/64

PHYSICAL AND CHEMICAL PROPERTIES OF REDUCED METAL HALIDES

A number of studies of reactions of metals with their molten halides have disclosed new and unusual solid phases requiring additional characterization of their structural stability or thermodynamic properties. Similar requirements pertain to the lower iodides of niobium, thorium and hafnium, particularly as they apply to their role in metal production.

Specifically, magnetic susceptibilities are being measured to establish (1) whether the phase $LaI_{2.4}$ contains La^{2+} ions or metal-like electrons and (2) the possible nature of the constituent ions in the unusual salt $GdCl_{1.6}$. Hall coefficient data are being obtained for the metallic $La^{3+}(I^-)_2e^-$ to supplement conductivity and susceptibility data. Also underway is a molecular orbital treatment of the bonding in Bi_5^{+} previously identified in $BiCl_{1.167}$.

An earlier study of the ThI_4-Th system disclosed the existence of a volatile $ThOI_2$. An improved synthesis of this compound is being developed, and this will be followed by measurement of its decomposition and vaporization equilibria. The pressures of gaseous niobium iodides in equilibrium with solid $NbI_{2.67}$ and Nb are being determined by static and transpiration techniques. Finally conventional phase studies are underway in the system HfI_4-Hf to establish the identity of the lower halides as well as to provide a possible analogue of the metallic $Th^{4+}(I^-)_2(e^-)_2$.

Publication

1. Clark and Corbett, "Preparation of Metallic Thorium Diiodide," Inorg. Chem. 2, 460 (1963).

1A20

AMES LABORATORY Chemistry Division

J. D. Corbett/B. N. Ramsey 1/10/64

REACTION OF METALS WITH THEIR MOLTEN HALIDES

The nature of the solutions formed by many metals in their molten halides presents a challenging problem in high temperature chemistry. Present work is directed particularly toward obtaining (1) further evidence for slightly stable, lower oxidation states commonly thought to be formed in many of these solutions, and (2) additional understanding of the unusual spectral and conductivity features of certain systems.

Specifically, the rare earth metal-metal halide systems have proven to be a fruitful area of investigation, and at present, phase relationships of the respective metals with Sc, Y, and Er chlorides and iodides are being examined. The temperature and concentration dependence of the electronic conductivity in halide solutions of La, Ce and Pr are being investigated to provide information on the electron exchange mechanism that is thought to take place between M^{2+} solute ions suggested by cryoscopic evidence and M^{3+} solvent cations.

Substitution of AlX_4^- for X^- in systems such as CdX_2-Cd is known to effect a substantial increase in the stability of the solute, Cd^{2+} in this case. The accompanying, marked change in the visible and UV spectra is being studied, and the reduction products of other $M(AlCl_4)_2$ salts (e.g., Pb, Ni) in $NaAlCl_4$ solvent are being studied by EMF methods.

Publication

1. Dworkin, Sallach, Bronstein, Bredig and Corbett, "The Electrical Conductivity of Solutions of Metals in Their Molten Halides. VI. Lanthanum, Cerium, Praseodynium, and Neodymium in Their Molten Iodides." J. Phys. Chem. 67 1145-1148 (1963).*

*Joint Study with ORNL.

1A21

AMES LABORATORY Chemistry Division

Hugo F. Franzen/John Smeggil 3/1/64

PHASE RELATION AND VAPORIZATION REACTIONS AT HIGH TEMPERATURES

The goals of this research are to describe high temperature condensed phase relations, to determine the thermodynamics of high temperature vaporization reactions, and to contribute to the understanding of the relationship between the nature of condensed phases and their mode of vaporization.

A study of the condensed phase relations in the hafnium-sulfur system is in progress. A study of the vaporization behavior of this system will follow. A study of the transition between the well known monosulfide of vanadium and the recently discovered substoichiometric monosulfide is in progress. A precise determination will be made of the lattice parameter *versus* composition curve.

A study of the transport of boron in bromine atmospheres under the influence of temperature gradients is being initiated. It is hoped that this study will produce fundamental information about the nature of the vaporization process, i.e. information about the nature of the reaction which occurs when gaseous bromine reacts with solid boron to produce gaseous boron tribromide.

1A22

AMES LABORATORY Chemistry Division

D. S. Martin, Jr. 3/1/64

CHEMICAL EFFECTS IN NUCLEAR REACTIONS

For (n,γ) and (γ,n) processes the radioactive nuclides produced are the same chemicsl elements as the target. Therefore if a target element is in a suitable chemical compound, recoil from the nuclear reaction may leave the radionuclide in a chemical form which can be separated from the bulk target element. The radioactivity may then be isolated with much reduced dilution by stable nuclides so that greater sensitivity in radiochemical techniques may be achieved. The identification of the particular chemical species which carries the radionuclides provides information about the reactions of the "hot" atoms recoiling from the nuclear neutrons with kinetic energy in excess of thermal energy. In some instances the activity is reincorporated into the target compound by thermal aging. The chemical identification of Co^{58} activity as Co^{++}, as the target compound, and as other general and specific Co^{III}-complexes is to be determined with the (γ,n) process on tris(ethylenediamine)cobalt(III), $Co(en)_3^{+3}$, and hexaamminecobalt(III), $Co(NH_3)_6^{+3}$, salts in the ISU synchrotron. Also, the exchange of W^{187} between metatungstate polymers and orthotungstate, WO_4^{-2}, is to be studied to determine if the polymers can possibly be used for this Szilard-Chalmers type of separation.

1A23

AMES LABORATORY Chemistry Division

D. S. Martin, Jr./Henry Abbink 3/1/64

PHYSICAL PROPERTIES OF SILVER HALIDES

The conductivity of silver halides is strongly dependent upon the impurity content, and the dependence of the conductivity upon temperature and impurity concentrations permits a test of theories and models for these ionic compounds. Silver chloride has been purified by fractional distillation at low pressures in a silica apparatus, and single crystals have been prepared from this pure material. The electrical conductivity of this material has indicated high purity. Single crystals of AgCl have also been prepared to which a small amount of either CuCl and $CdCl_2$ has been added. Neutron activation analyses are being utilized to analyze these crystals in order to attain the necessary sensitivity, and an evaluation of the electrical conductivity as a function of temperature and concentration is under way.

AMES LABORATORY Chemistry Division

D. S. Martin, Jr./R. C. Tucker 1/10/64

CHEMISTRY OF THE PLATINUM ELEMENTS

The platinum metals form a group of elements with striking resistance to corrosion, high temperatures and chemical catalytic activity. Their compounds possess a wide range of chemical and physical properties which are important in separation processes and in fundamental considerations of chemical bonding.

The rates of substitution for halide ligands in a series of complexes of platinum(II) by water, hydroxide, ammonia and halide groups are being determined by spectrophotometric and conductimetric methods together with isotopic tracer techniques. Current emphasis is being given to the reactions of trichloroammineplatinate(II) ion, $(Pt(NH_3)Cl_3)^-$, dichloro(ethylenediamine)platinate(II), $(Pt(en)Cl_2)$ and the sym-trans-μ-dichloro-dichlorobis(ethylene)diplatinum(II), $(Pt(C_2H_4)Cl_2)_2$.

The ultraviolet and visible absorption spectra provide important information about the electronic transition of these complexes. The determination of these spectra in single crystals with polarized light of $PtCl_4^{-2}$ has provided a definitive identification of the excited states of this ion. The theoretical treatment developed for this ion provides a significant development in the considerations of these spectra so additional efforts are being directed toward improving techniques for obtaining crystal spectra.

Procedures are under development for the determination by activation analysis of each of the platinum metals in specimens of the various elements. Since the presence of small amounts of these elements frequently alter chemical properties, one objective will be the attainment of maximum sensitivity.

Publication

1. Lokken, Martin, "Exchange and Substitution Reactions of Platinum(II) Complexes. IX. Trichloro(ethylene)platinate(II)", Inorg. Chem. 2, 562-568 (1963).

1A25

AMES LABORATORY Chemistry Division

Jack E. Powell/Harvey Burkholder 3/1/64

SEPARATION OF RARE EARTHS BY ION EXCHANGE

Isolation of individual rare earths in a highly pure form continues to be an important and challenging problem. The search for more efficient methods than are presently used for isolating the less abundant rare earth elements: Lutetium, thulium, terbium and europium. It is believed that the current methods of separation and isolation can be improved substantially by employing better combinations of existing procedures and by incorporating new techniques based on fundamental data obtained from measurement of chelate stability constants. The effects of operating at elevated temperature are also being investigated. In order to evaluate new schemes effectively, larger-than-laboratory-scale experiments are necessary to learn about potential scale up problems.

1A26

AMES LABORATORY Chemistry Division

Jack E. Powell/Duane Nowlin 3/1/64

SEPARATION OF LIGHT ISOTOPES

The separation of isotopes of light elements from one another by ion exchange and continuous countercurrent liquid-liquid extraction is important from both fundamental and practical points of view. The most fruitful approach to study isotope separation appears to lie in the direction of small-scale dynamic equilibrium studies which furnish unequivocal answers as to the ultimate separation factors that can be had in various chemical exchange systems.

In the past, such studies have been successful in establishing the practicality of enriching nitrogen-15 in ammonia and various amine ion exchange systems, the enriching of lithium-6 on cation exchange resins and the enriching of sulfur isotopes by anion exchange. Present plans include the investigation of countercurrent means of separating chlorine-35 and chlorine-37, and further study of chemical exchange systems for separating sulfur isotopes.

In addition to separation factors, dynamic equilibrium studies on ion exchange columns provide information about theoretical plate heights and chemical stability, both of which are essential for evaluating practical applications.

1A27

AMES LABORATORY Chemistry Division

J. E. Powell/A. Gupta/J. Farrell/Y. Suzuki 3/1/64

DETERMINATION OF STABILITY CONSTANTS OF RARE EARTH COMPLEX SPECIES

Formation constant sequences and related data for the individual complex species formed between the lanthanons, yttrium and scandium and various organic ligands are of both theoretical and practical value to scientists interested in chelation and coordination theories and in the efficient separation of rare earths by ion exchange, solvent extraction or fractional precipitation for either preparative or analytical reasons.

The list of ligands investigated recently at Ames includes propionate, isobutyrate, thioglycolate, methoxyacetate, glycolate, lactate, α-hydroxyisobutyrate, glyoxylate, benzilate, tricarballylate, trimethyllactate, trihydroxyisobutyrate and 2,3-dihydroxy-2-methylbutyrate. From information obtained from, and anomalies observed in some of these stability sequences, it appears that many additional homologues and analogues of α-hydroxycarboxylic acids merit investigation as to their potential as chelating agents for rare earths and yttrium. Some of the ligands to be studied, of necessity, will have to be synthesized in the laboratory.

Publications

1. Kolat and Powell, "The Solid Rare-Earth Chelates of Ethylenediaminetetraacetic Acid", J. Inorg. Chem., 1, 485-490 (1962).

2. Gupta and Powell, "Formation Constants of the Complex Species Formed by Interaction of Rare Earth N-Hydroxy-Ethylethylenediamine-N,N,N,=triacetate Complexes with an Equivalent Amount of Base", J. Inorg. Chem., 1, 955-956 (1963).

AMES LABORATORY Chemistry Division

A. F. Voigt/R. G. Clark/W. A. Stensland/E. C. Jacobsen 3/1/64

HIGH PURITY MATERIALS STUDIES USING ACTIVATION ANALYSIS FOR IMPURITY DETERMINATION

The use of neutron activation is being investigated as an analytical tool for problems in the development of materials of high purity and known composition. Thermal neutrons from reactors have been used in the analysis for sodium in the sodium tungsten bronzes. Current problems include the determination of tantalum impurity in thorium and rare earths, of rare earths in each other and in yttrium, of impurities from container materials in various metals and ceramics.

A 14 Mev neutron generator has been installed and is being applied to the determination of oxygen by the reaction O^{16} $(n,p)N^{16}$(7 sec.) A programmed rapid delivery system is used to give the sample an irradiation of fixed duration followed by delivery to the counter and recording of counts for a fixed period. The method will be applied to various metals as a check on spectroscopic and vacuum fusion techniques and to other metals to which these procedures cannot be applied. The determination of other light element impurities will also be studied.

Much of the future program will involve the use of the Ames Laboratory Research Reactor when it becomes available during the next year.

Publication

1. Reuland and Voigt, "Activation Analysis for Sodium Tungsten Bronzes", Anal. Chem. 35, 1263 (1963).

AMES LABORATORY Chemistry Division

A. F. Voigt/D. B. DeVries/D. E. Clark/F. G. Mesich 3/1/64

RECOIL CHEMISTRY OF CARBON-11

The behavior of atoms with energies greater than those of the surrounding molecules is related to the understanding of the interaction of energy and matter. Of particular interest is the behavior of carbon in organic molecules since carbon chains form the skeleton of the molecules. The availability of a synchrotron in which the 20 min. C^{11} can be produced by the $C^{12}(\gamma,n)$ reaction and of rapid gas chromatographic separation have made it possible to study the behavior of high energy carbon atoms as they enter into chemical combination. For hydrocarbons with six carbon atoms as targets: benzene, cyclohexane, normal and branched hexanes, the products of lower molecular weight have been characterized and their yields correlated with reaction mechanisms. In all cases the most abundant gaseous product is acetylene. Its yield is unaffected by iodine scavenger while those of other gases, methane, ethane, ethylene, are reduced. Results support a bond-insertion mechanism in which the energetic carbon combines with the parent molecule but contributes sufficient energy to the intermediate to cause C-C bonds to break. With this mechanism molecules with seven carbons should also result. The first experiments designed to observe the latter indicate they are formed in high yield. This portion of the products will be examined in more detail. In other future work other types of molecules will be irradiated and absolute yields determined.

Publication

1. Rack, Lang and Voigt, "Influence of Structure on Gaseous Products from C^{11} Recoil Reactions of Hydrocarbons", J. Chem. Phys. 38, 1211 (1963).

1B2

AMES LABORATORY Chemical Engineering Division

Lawrence Burkhart/Rowland Felt 1/10/64

FUSED SALT-MOLTEN METAL EXTRACTION

Fused salt-molten metal extraction has been proposed as a method for reprocessing nuclear reactor fuel. It also appears to be useful for pure metal production, and perhaps for other chemical processing operations. Fused salts possess many unique properties for high temperature processing. They are liquid over a wide temperature range, have a low vapor pressure, good electrical conductivity, and low viscosity.

Although considerable effort is being devoted to fused salt chemistry, not much attention has been given to fused salt-molten metal processing. In this project a multistage fused salt-molten metal extractor has been operated at 220°C to separate cadmium from a lead-bismuth eutectic using a sodium-potassium-zinc chloride eutectic salt mixture. The most important factors in fused salt-molten metal extraction equipment are agitation and drop size. Limiting resistances in the transfer process are probably diffusion through the metal phase and the formation of oxide or other films at the salt-metal interface. The presence of reaction products at the interface may also shift the equilibrium constant to a different value from that calculated for the bulk phases. Kinetic studies of the transfer process are continuing since this seems to be the most immediate problem in the proper design of such extraction equipment.

SECTION 1B

AMES LABORATORY - CHEMICAL ENGINEERING DIVISION

1B1 Mass Transfer Through A Changing Interface: Extraction From Forming and Collapsing Drops

1B2 Fused Salt-Molten Metal Extraction

1B3 Laminar Flow Heat Transfer in the Thermal Entry Region at Low Peclet Numbers

1B4 Thermodynamic Properties of Liquid Metal Systems

1B5 Liquid Metal Vaporization

1B6 Liquid Metal Distillation

1B7 Turbulent Transport of Heat, Mass, and Momentum

1B8 Separation of Rare Earths by Solvent Extraction

1B9 Halogenation Studies

For further information on work completed, the reader is referred to the open scientific literature and to the Ames Laboratory Annual Summary Report for July 1962 through June 1963, IS-700, September, 1963.

AMES LABORATORY Chemical Engineering Division

L. Burkhart/W. Scholle/J. San Giovanni/H. Torrey 1/10/64

MASS TRANSFER THROUGH A CHANGING INTERFACE: EXTRACTION FROM FORMING AND COLLAPSING DROPS

Mass transfer studies are being made for solute diffusing through a changing interface, during droplet formation and collapse. Three models for the mass transfer process under these conditions have been tested -- a molecular diffusion model, a surface renewal model and a cellular renewal model. All three are much too simplified to describe the mass transfer process under these conditions, particularly when they do not account for the possibility of interfacial turbulence.

For identical experiments on mass transfer from forming droplets, the presence of interfacial turbulence has been shown to give a 30 to 35 percent increase in mass transfer.

Analysis of flow patterns within a forming and collapsing drop from both mathematical and experimental data is being used to clarify the type of model to be used for mass transport within the droplet. Dynamic measurement of mass transfer from a rising droplet will provide continuous concentration data as a function of column position and will minimize extrapolation techniques in determining the relative importance of drop formation and drop rise time on mass transfer.

Single drop studies will be extended to extraction from orifice plates to obtain information for filling the gap in research between single droplet extraction studies, and work involving perforated plates with many holes.

Publication:

1. Honekamp and Burkhart, "Role of the Packing in a Scheibel Extractor," Ind. Eng. Chem., Process Design and Development Section, 1, 176 (1962).

AMES LABORATORY Chemical Engineering Division

Lawrence Burkhart/Kermit Holman/Robert Huang 1/10/64

LAMINAR FLOW HEAT TRANSFER IN THE THERMAL ENTRY REGION AT LOW PECLET NUMBERS

The energy equation, including axial conduction, is being studied for heat transfer to fluids with constant wall heat flux or constant wall temperature.

The constant wall heat flux model is solved by superposition of two solutions, one a fully developed heat transfer solution and the other an arbitrary function of the radial and axial independent variables. A generalized Sturm-Liouville system results and the eigenfunctions are expanded in a Bessel series. For the fully developed laminar flow models, a finite Hankel transform of the eigenfunction expansion generates an infinite system of algebraic equations for the eigenvalues and associated coefficients which are found by iteration. For the plug flow models no iteration is required.

Neglecting axial conduction at Peclet numbers less than 100 can produce errors in estimating the thermal entry region, the wall temperature distribution, or the amount of heat transfer. For the constant wall temperature models over fifty percent of the total heat transport can occur in the thermal entry region.

The results bear most particularly on heat transfer to liquid metals. Direct numerical solution of the energy equation is being studied to compare its efficiency with the eigenvalue approach, since the equations occur in several areas of chemical engineering and are usually difficult to solve.

AMES LABORATORY Chemical Engineering Division

George Burnet/F. D. Stevenson/T. Lenz/K. Walter 1/10/64

THERMODYNAMIC PROPERTIES OF LIQUID METAL SYSTEMS

The uncertainty of liquid metal distillation rates is due in part to the non-ideality of the alloy melts. A study of the thermodynamic properties of binary liquid metal systems confirms that improved rate predictions should be based on component activities rather than mole fractions. Current work on activity coefficient measurements is based on Langmuir's evaporation rate theory coupled with calculations using the Gibbs-Duhem equation. During the next year, measurements will be obtained on (a) binary systems with one component essentially non-volatile compared to the other and (b) binary systems with two volatile components.

The activity coefficients of the volatile component of case (a) systems will be obtained as a function of composition by a technique of simultaneous vaporization of a series of alloys. The present work is concerned with the tin-thallium system, with emphasis upon obtaining better understanding of the effect of surface conditions. If the method proves successful for binary systems, it could then be extended to ternary systems of one volatile component.

The technique of simultaneous vaporization of a series of alloys will also be used for measuring the activity coefficients of case (b) systems. In addition to measuring the rate of sample weight loss, the vapor phase composition will be established by radioactive tracers. This approach also may be extended to ternary systems of two and, possibly, three components of similar volatility.

AMES LABORATORY Chemical Engineering Division

George Burnet/William Walsh/Charles Buell 1/10/64

LIQUID METAL VAPORIZATION

Liquid metals vary greatly in vapor pressure and should be capable of being separated by distillation. Little is known, however, about the vaporization of liquid metal mixtures. One of the important questions yet to be answered is the extent to which the surface becomes depleted in the more volatile components. Diffusion of these components from the bulk of the liquid to the surface may well be the rate-controlling step in the process.

A high-vacuum device has been built and successfully operated which utilizes X-ray fluorescence to measure the concentration of metal ions immediately at the surface of a liquid melt. Tests conducted with the zinc-tin system have demonstrated a high degree of precision and reproducibility over the concentration range of 0 to 50% zinc.

An actual distillation conducted at 400°C showed a nearly linear reduction in zinc (the more volatile component) concentration at the surface with time. The final zinc concentration at the surface was less than that in the bulk. This is the first experimental verification of surface depletion during the vaporization of a liquid metal mixture. The effect of distillation rate and surface oxide films will be investigated, and the technique used to measure liquid phase diffusivities.

AMES LABORATORY Chemical Engineering Division

George Burnet/Lawrence Murdoch 1/10/64

LIQUID METAL DISTILLATION

Major difficulties encountered in separation by distillation are suitable container materials, techniques for assembling separate pieces of equipment, maintenance of high vacuum, and condensation and removal of the product from the system.

A procedure has been developed for screening a large number of container materials to determine their corrosion resistance when exposed to liquid metals under flow conditions. Trace amounts of certain metals have been found to provide corrosion resistance in some systems. A special flange assembly for liquid metal service and a liquid-metal cooled condenser have been developed.

The above work has lead to the construction of a loop through which liquid metal mixtures can be circulated using a diaphragm pump. Installed in the loop is a single-stage flash distillation chamber which has given separation efficiencies higher than any previously reported. Flash chamber design, operating temperature, and feed concentration are to be investigated.

Publication

1. Burnet and Clifford, "Attack of Ferritic Steels by the Eutectic Melt of Lead-Bismuth," Chem. Eng. Progr. Symposium Series, 39, 104-107 (1962).

AMES LABORATORY Chemical Engineering Division

R. Fahien/W. Blumenberg/W. Crowe/D. Shuck/M. Halberg 1/10/64

TURBULENT TRANSPORT OF HEAT, MASS, AND MOMENTUM

The design and operation of equipment for the separation of fission products as well as the design of nuclear reactors and their auxiliary equipment requires the prediction of the rates of transfer of heat, materials, and fluid momentum. Present methods for calculating these rates are not satisfactory because they only approximately handle the different effects that occur under conditions of practical interest.

An experimental program has been undertaken to determine the eddy diffusivities--quantities that are measures of the rate of transport of heat, mass and momentum under turbulent flow--as a function of flow velocity and properties of the fluid. These experiments have been carried out for

a) Mass transport in liquids (Radial, axial, and angular components of the eddy diffusivity tensor as functions of position),

b) Mass transport in gases,

c) Heat transport in liquids, and

d) Mass transport in liquids and gases flowing through packed columns.

Theoretical work has been carried out on the prediction of heat, mass, and momentum transport together with other work on the design of equipment through the use of these quantities.

AMES LABORATORY Chemical Engineering Division

Morton Smutz/Totaro Goto 1/10/64

SEPARATION OF RARE EARTHS BY SOLVENT EXTRACTION

The separation of the individual rare earths from one another by continuous countercurrent liquid-liquid extraction is an important problem from both a fundamental and an applied point of view. The chemistry involved in the aqueous and organic phases is not well understood and thus the selection of solvents and the operating conditions have been largely a matter of trial-and-error. As the chemistry involved with the rare earth salts as solutes is known to be similar to that observed in actinide and other systems, the results of this research will be of great interest to all working in the field of solvent extraction chemistry.

Precise equilibrium data are being obtained using organophosphate solvents such as TBP and D2EHPA with rare earth nitrates and chlorides. The data are being correlated for use in predicting equilibria for multicomponent systems. Stage-by-stage calculation methods are being developed, and the accuracy of prediction methods are being checked against data obtained in simulated column runs and continuous runs in a pulse column.

Emphasis is being given to a study of the species present in the aqueous phase because this appears to be the key to an understanding of the observed equilibrium distribution data.

AMES LABORATORY Chemical Engineering Division

F. D. Stevenson/D. Boesiger/J. Conway/D. Lorine 1/10/64

HALOGENATION STUDIES

The separation of niobium from tantalum by halogenation processing is complicated by two problems: (1) the halides of niobium and tantalum are very similar both physically (vapor pressure) and chemically and (2) undesirable niobium oxychloride is formed with the desired niobium pentachloride during the initial chlorination step.

Work is underway to study the complexing tendencies of tantalum and niobium chlorides with calcium fluoride. According to previous work, separation of niobium and tantalum is enhanced by CaF_2 addition. The relative volatilities of complex halides often differ significantly and could provide the volatility differences necessary for the separation. Physical and chemical properties of the reaction products, after isolation under carefully controlled conditions, will be used to confirm complex formation. Future work could lead to investigations with other alkali and alkaline earth halides and with different metal systems.

A kinetic study of the rechlorination of niobium oxychloride is in progress to establish the extent of conversion, reaction mechanism, and the reaction rate as a function of temperature. An isothermal flow reactor will be used to react chlorine with the vaporized niobium oxychloride in a packed carbon bed. The use of different chlorination and reduction agents may lead to more satisfactory conversions. The effect of pressure may also be studied depending on the mechanism of the reaction.

SECTION 2A

ARGONNE NATIONAL LABORATORY

2A1 Nuclear Reactions

2A2 High Resolution Studies of (p,p') and (p,α) Reactions in the Mass Region $A = 50$ to 60

2A3 Isomeric Cross Section Ratio Studies

2A4 Investigation of Evaporation Spectra in Nuclear Reactions

2A5 Study of Nuclear Structure through the $(\alpha,\alpha' f)$ Reaction

2A6 Investigation of Fluctuations in Nuclear Reaction Cross Sections Leading to Specific Final States

2A7 Nuclear Properties of the Heavy Elements

2A8 Neutron Cross Sections of the Actinide Elements

2A9 Study of Fission-Spallation Reactions in Heavy Elements

2A10 Range-Energy Relations for Heavy Recoil Fragments of High Energy Nuclear Reactions

2A11 Differential Recoil Study of the $C^{12}(p,pn)C^{11}$ Reaction

2A12 Radiochemical Studies of Nuclear Reactions Resulting from Muon Capture

2A13 The Investigation of $(p,p\pi^{+})$ Reactions

2A14 Fission Process Studies

2A15 Investigation of the Near-Threshold Fission of U^{235} by Means of the $U^{234}(d,pf)$ Reaction

2A16 Recoil Studies of Nuclear Reactions Induced by High Energy Particles. I. The Production of Tb^{149}

2A17 Investigations of Gamma Rays and Neutrons Emitted From Fission Fragments

2A18 Fission Studies

2A19 Kinetic Energy Correlations

2A20 Fission Properties of the Actinide Elements

2A21 Half-Lives and Decay Schemes

SECTION 2A (Continued)

2A22 Nuclear Decay Schemes

2A23 Beta Ray Spectrometry

2A24 Computer Analysis of Beta Spectra

2A25 Beta-Spectral Shape of the Sb^{122} Decay

2A26 Liquid Scintillator Studies

2A27 Nuclear Chemistry

2A28 Light Element Analysis by Rutherford Scattering

2A29 Geo-Cosmochemistry

2A30 Mineralogical and Chemical Analyses of Meteorites

2A31 Search for Element 61 in Nature

2A32 Analysis by Differential Migration

2A33 Isotopic Source Neutron Facility

2A34 Non-Destructive Activation Analysis

2A35 Emission Spectrographic Analysis

2A36 Development of Oxygen Analysis Methods

2A37 Uranium Isotope Investigations by Atomic Absorption Spectrophotometry

2A38 Inelastic Collision Processes of MeV Ions

2A39 Crossed-Beam Studies of Reactions of Accelerated Atoms with Molecules

2A40 Organic Solid State Radiation Chemistry

2A41 The Solvated Electron and Molecular Ions in Polar Organic Liquids

2A42 Reactions of the Hydrated Electron and the Hydroxyl Radical

2A43 Spectra of Radiation Induced Transient Species in Aqueous Solutions

2A44 Radiation Chemistry - Pulsed Radiolysis

SECTION 2A (Continued)

2A68 Mass Spectrometric Studies of Noble Gas Compounds

2A69 Theoretical Nuclear Chemistry

2A70 Theoretical Studies of Simple Nuclear Reactions at High Energy

2A71 X-Ray Diffraction Studies

2A72 Emission Spectroscopy

2A73 Magnetic Resonance Studies

2A74 Neutron Diffraction Studies

2A75 Theoretical Studies in Molecular Quantum Mechanics

2A76 Theoretical Investigations of the Spectroscopic Properties of Atoms and Ions

2A77 Asymmetric Rotor Nuclear Model

2A78 Uranium-Oxygen Bonding

2A79 Properties of Liquid Helium-3 and Liquid Helium-4 At Low Temperatures

2A80 Low Temperature Calorimetry

2A81 Ion-Ion and Ion-Solvent Interactions

2A82 Inter- and Intramolecular Hydrogen Bonding in Aqueous Solution, Metal Ion Chelate Complexes, and the pH Scale

2A83 Magnetic Susceptibility Studies

2A84 Application of Nuclear Magnetic Resonance to the Study of Structure in Electrolyte Solutions

2A85 Research Applications of Mass Spectrometry

2A86 The Physical Chemistry of the Interaction of (X) (Y)PO(OH) Extractants with Hydrogen Bond Donors and Acceptors

2A87 Physical Chemistry of Acidic Organophosphorus Compounds and Various Inorganic Salts

SECTION 2A (Continued)

2A68 Mass Spectrometric Studies of Noble Gas Compounds

2A69 Theoretical Nuclear Chemistry

2A70 Theoretical Studies of Simple Nuclear Reactions at High Energy

2A71 X-Ray Diffraction Studies

2A72 Emission Spectroscopy

2A73 Magnetic Resonance Studies

2A74 Neutron Diffraction Studies

2A75 Theoretical Studies in Molecular Quantum Mechanics

2A76 Theoretical Investigations of the Spectroscopic Properties of Atoms and Ions

2A77 Asymmetric Rotor Nuclear Model

2A78 Uranium-Oxygen Bonding

2A79 Properties of Liquid Helium-3 and Liquid Helium-4 At Low Temperatures

2A80 Low Temperature Calorimetry

2A81 Ion-Ion and Ion-Solvent Interactions

2A82 Inter- and Intramolecular Hydrogen Bonding in Aqueous Solution, Metal Ion Chelate Complexes, and the pH Scale

2A83 Magnetic Susceptibility Studies

2A84 Application of Nuclear Magnetic Resonance to the Study of Structure in Electrolyte Solutions

2A85 Research Applications of Mass Spectrometry

2A86 The Physical Chemistry of the Interaction of (X) (Y)PO(OH) Extractants with Hydrogen Bond Donors and Acceptors

2A87 Physical Chemistry of Acidic Organophosphorus Compounds and Various Inorganic Salts

2A88 The Acid Strength of (X)(Y)PO(OH) and its Extractant Effectiveness as a Function of X and Y

2A89 Applicability of (X)(Y)PO(OH) Extractants to Actinide and Lanthanide Separations as a Function of X and Y

2A90 Transplutonium Element Separations Chemistry

For further information on completed work, the reader is referred to the open scientific literature.

ARGONNE NATIONAL LABORATORY Chemistry Division

P. R. Fields/A. M. Friedman/J. Milsted/
R. Sjoblom/R. Barnes 3/26/64

NUCLEAR REACTIONS

The availability of the 60" Argonne Cyclotron, CP-5 Research Reactor, a 3 MeV Van de Graaff, a LINAC, and a Tandem Van de Graaff makes it possible to study a wide variety of nuclear reactions. A Li^{+3} beam has been used in the 60" cyclotron to prepare the delayed proton emitter, Ne^{17} and the delayed α emitter Ga^{62} as well as to produce other neutron deficient nuclides. Several isotopes have been prepared for nuclear studies by double alpha particle irradiations, e.g. $U^{235}(\alpha,3n)\ Pu^{236}(\alpha,2n)\ Cm^{238}$. A general study of transfer and stripping reactions is in progress. Some transfer reactions were carried out using the Yale HILAC. A recent development in the theory of single nucleon transfer reactions shows promise. An excellent fit between theory and experiment was obtained for $Pb^{208}\ (He^4,He^3)\ Pb^{209}$.

The LINAC has been and will be used to measure (γ,f) thresholds of many heavy nuclides e.g. Bk^{249}, Pu^{240}, Pu^{242} etc. Some (γ,n) and (γ,p) yields have also been investigated.

A program has been activated to study He^3 reactions such as compound nucleus formation, and the many different stripping reactions as soon as the He^3 beam is developed early this year in the 60" cyclotron.

A search for spontaneous fission in excited isomeric states of the actinide elements is in progress. Attempts are being made to prepare these states by irradiating U, Np, Pu and Am isotopes with high energy helium ions and deuterons.

Also underway are neutron irradiations of actinides to produce isomeric states and to study the cross sections for the production of different isomeric states. In addition, isomeric states and their properties are being studied by producing these states via gamma irradiation. A study is being made of nuclear levels, and level widths by studying excitation functions with the 3 MeV Van de Graaff.

Publication:

A. M. Friedman and P. Benioff, "Single Neutron Transfer Reactions," Proceedings of Int. Conf. on Direct Interactions, Padua (1963).

ARGONNE NATIONAL LABORATORY Chemistry Division

J. R. Huizenga/A. Katsanos[*]/H. K. Vonach[†] 3/26/64

HIGH RESOLUTION STUDIES OF (p,p') AND (p,α) REACTIONS IN THE MASS REGION A = 50 TO 60

The broad range magnetic spectrograph associated with the Argonne tandem Van de Graaff is being used to study nuclear levels produced in the (p,p') and (p,α) reactions. In many cases a large enough number of residual states can be resolved to make a statistical analysis in terms of a continuous level density. To date we have studied the following reactions: $Co^{59}(p,\alpha)Fe^{56}$, $Mn^{55}(p,\alpha)Cr^{52}$, $Fe^{56}(p,p')$, $Mn^{55}(p,p')$ and $Co^{59}(p,p')$. A resolution (FWHM) of 6 to 9 keV has been obtained in the (p,p') measurements and final states in Fe^{56} have been resolved with excitation energy up to 6 MeV. The level density determined by this direct counting method is being compared with other less direct determinations of the level density for the same range of excitation energy. In a number of cases it is hoped that this comparison will give some information about the uncertainties involved in these indirect determinations of the level density.

In the future we tentatively plan to extend these measurements to heavier nuclei. However, due to the decrease in cross section for charged particle emission and the increase in level density with A, the feasibility of this extension has to be investigated.

[*] University of Chicago, Chicago, Illinois

[†] Institut fur Radiumforschung und Kernphysik, Vienna, Austria

ARGONNE NATIONAL LABORATORY Chemistry Division

J. R. Huizenga/R. Vandenbosch[*]/H. K. Vonach[†]/J. Wing 3/26/64

ISOMERIC CROSS SECTION RATIO STUDIES

In previous work at this Laboratory a statistical model was developed to interpret experimental isomeric cross section data and to obtain information about the angular momentum dependence of the nuclear level density. Further experiments to test this model are in progress or have been completed. Recent experimental work in this field include measurements of isomer ratios from reactions induced with the tandem Van de Graaff which provides beams of accurately known energy.

The theoretical calculation of isomer ratios have been extended to include calculations with a semi-quantitative theory for a Fermi gas with pairing correlations analogous to those of a superconducting metal. The superconductor model predicts a reduction from the Fermi gas rigid-body moment of inertia which is consistent with experimental isomer ratios for nuclei with an odd number of nucleons. However, the superconductor model overestimates the reduction in the moment of inertia for odd-odd nuclei. A manuscript "Interpretation of Isomer Ratios in Nuclear Reactions with Fermi-Gas and Superconductor Models" has just been submitted for publication in Nuclear Physics.

Publications:

H. K. Vonach, R. Vandenbosch and J. R. Huizenga, "Interpretation of Isomer Ratios in Nuclear Reactions with Fermi Gas and Superconductor Models," in press, Nuclear Physics, (1964).

C. T. Bishop, J. R. Huizenga and J. P. Hummel, "Isomer Ratios from (α,xn) Reactions in Silver," in press, Physical Review (1964).

[*] Department of Chemistry, University of Washington, Seattle, Washington

[†] Institut fur Radiumforschung und Kernphysik, Vienna, Austria

ARGONNE NATIONAL LABORATORY Chemistry Division

J. R. Huizenga/H. K. Vonach* 3/26/64

INVESTIGATION OF EVAPORATION SPECTRA IN NUCLEAR REACTIONS

Decay of the compound nucleus Ni^{60} has been studied through the $Co^{59}(p,\alpha)Fe^{56}$ reaction. Energy spectra of α-particles from this reaction were measured for protons accelerated in the Argonne tandem Van de Graaff over the energy range 7 to 13.5 MeV. The α-spectra were obtained with surface barrier detectors at 90° and 170° to the beam direction. The cross section ratio $\sigma(170^\circ)/\sigma(90^\circ)$ was determined to an accuracy of 3% as a function of both the alpha particle energy and the proton bombarding energy, and the results were analyzed in terms of the statistical theory. The angular anisotropy of the alpha particles is accounted for by only a small reduction of the moment of inertia from its rigid-body value. A nuclear temperature of 1.4 MeV was derived from the shape of the alpha particle spectra. The temperature is constant over the whole range of excitation energies which were investigated and independent of bombarding energy.

A similar investigation of the reaction $Fe^{56}(\alpha,\alpha')$ is in progress. The proton spectra emitted by the Ni^{60} compound nucleus formed in the two above reactions will also be investigated. Furthermore, Mr. A. Katsanos (graduate student from University of Chicago) has begun a similar study for the systems (Mn^{55}+p) and (Cr^{52}+α).

Publication:

H. Vonach and J. R. Huizenga, "Study of the $Co^{59}(p,\alpha)Fe^{56}$ Reaction," Bulletin of American Physical Society 9, 168 (1964).

---

*Institut fur Radiumforschung und Kernphysik, Vienna, Austria

2A5

ARGONNE NATIONAL LABORATORY Chemistry Division

J. R. Huizenga/B. D. Wilkins*/J. P. Unik 3/26/64

STUDY OF NUCLEAR STRUCTURE THROUGH THE $(\alpha,\alpha'f)$ REACTION

An experimental program is underway to study the $(\alpha,\alpha'f)$ reaction. The first experiments include the measurement of the angular correlation of fission fragments for even-even targets. The $(\alpha,\alpha'f)$ reaction allows one to investigate the interesting region near the fission threshold. Since the fissioning nucleus near threshold is relatively "cold," the saddle point is expected to have a level structure similar to that observed for the ground state deformation. For even-even nuclei where the excitation of intrinsic states requires breaking a nucleon pair, the lowest energy states are expected to be collective rotational and vibrational states.

Preliminary values of the angular dependent differential fission cross section for the $U^{238}(\alpha,\alpha'f)$ reaction have been obtained as a function of the α' energy. For the maximum energy α' group the angular dependent differential fission cross section is well represented by $1/\sin\theta$ with a measured ratio of about 10 for the maximum to minimum cross section. Such a sharp angular distribution is consistent with fissioning states of $K = 0$, and makes it possible to accurately determine the symmetry axis for possible distinction between various theoretical predictions.

The preliminary information obtained from this reaction is very promising and plans are underway to study the reaction in considerably more detail as well as to extend the measurements to other targets. This experiment requires a high resolution cyclotron for separation of some of the collective levels at the saddle point. The study of these levels for the highly deformed saddle configuration adds interesting new possibilities for probing nuclear structure.

Experiments are also planned to investigate long range α particles from fission.

---

*University of California, Berkeley, California

ARGONNE NATIONAL LABORATORY **Chemistry Division**

J. R. Huizenga/H. K. Vonach* 3/26/64

INVESTIGATION OF FLUCTUATIONS IN NUCLEAR REACTION CROSS SECTIONS LEADING TO SPECIFIC FINAL STATES

Recent theoretical investigations by Ericson and Brink have shown that the fluctuations in the cross sections of nuclear reactions in the excitation energy region of strongly overlapping levels in the compound nucleus can yield important information about nuclear reactions.

We have investigated these fluctuations in the excitation functions of the ground and several excited states in Fe^{56} produced in the $Co^{59}(p,\alpha)Fe^{56}$ reaction. Measurements of the differential cross sections of the α-groups at 90° and 170° to the beam direction were made in 10-keV steps with a target of 5-keV thickness for two proton energy regions, 7.90 to 8.10 MeV and 10.90 to 11.10 MeV.

The dependence of the amplitude of the fluctuations on angle and spin of the final state, as well as the absence of cross-correlations between different final states is qualitatively in agreement with the earlier mentioned theory. Analysis of the data in terms of a correlation function gives an upper limit of 10 keV for the width of the compound nuclear states. Making use of this value in conjunction with statistical model calculations enables one to estimate the level density of the compound nucleus at an excitation energy of approximately 20 MeV.

These measurements will be extended to larger energy intervals in order to improve the statistical accuracy of the analysis. In addition, we plan to study the angular dependence of the fluctuations in more detail, and to extend the studies to other reactions and targets.

Publication:

H. K Vonach and J. R. Huizenga, "Ericson Fluctuations in the $Co^{59}(p,\alpha)Fe^{56}$ Reaction," Bulletin, American Physical Society, Washington Meeting, (1964).

---

*Institut fur Radiumforschung und Kernphysik, Vienna, Austria

ARGONNE NATIONAL LABORATORY Chemistry Division

P. R. Fields/A. M. Friedman/H. Diamond/
J. Milsted/D. N. Metta 3/26/64

NUCLEAR PROPERTIES OF THE HEAVY ELEMENTS

The nuclear properties such as alpha energies and half lives, spontaneous fission half lives, β decay and electron capture energies and half lives, and the systematic behavior of these properties in the heavy element region are constantly being investigated. Many different techniques are employed, such as specific activity determinations, mass spectrometry, and decay over a period of time. Correlation with theories are also sought.

Detailed investigations of the decay schemes of heavy elements are also carried out, particularly alpha decay, with the aid of solid state detectors. Bk^{245}, Bk^{247}, Bk^{248}, Bk^{249}, Cf^{246} and Cf^{248} are recent isotopes which have been investigated. In the near future Cm^{246}, Cm^{248}, Cm^{240}, Cm^{241} and Cf^{251} will be examined.

A search is underway for nuclear isomerism in the heavy element region. Among the odd neutron - odd proton nuclides, Am^{244} and Bk^{248} have been demonstrated to possess long lived isomers. Other possible isomers are being investigated, as for example, Am^{246}, Bk^{246}, and Ac^{228}.

In some cases where the half lives appear to be very long, as for example, Pu^{244} and Cm^{247}, the possible geochemical significance is investigated.

Publications:

R. Vandenbosch, P. R. Fields, S. E. Vandenbosch, and D. Metta, "Search for a Spontaneous Fission Branch in a Metastable State of Cm^{244}," J. Inorg. and Nucl. Chem., 26, 219 (1964).

A. M. Friedman and J. Milsted, "Alpha Decay of Cf^{246}," Phys. Rev. 131, 772 (1963).

J. Milsted, A. M. Friedman and C. M. Stevens, "The Alpha Half-Life of Bk^{247}; A New Long-Lived Isomer of Bk^{248}," to be published, Phys. Rev.

ARGONNE NATIONAL LABORATORY Chemistry Division

P. R. Fields/H. Diamond/R. J. Barnes/
R. Sjoblom/J. Milsted

3/26/64

NEUTRON CROSS SECTIONS OF THE ACTINIDE ELEMENTS

The neutron cross sections of the actinide elements are quite important in order to calculate the rate of formation of these elements and their various isotopes in reactor irradiations and also to evaluate the effect on reactivity of actinide elements which are produced in fuel materials during reactor operations. In cooperation with the Physics Division the neutron cross sections of many actinide elements have been studied as a function of neutron energy using the Argonne Fast Chopper. Th^{229}, Th^{230}, Pu^{242}, Am^{243}, Cm^{244}, and Cm^{246} have recently been studied in this manner. This type of study yields the parameters describing the neutron resonances in the energy range 0.01 to 900 e.v. and thermal neutron cross sections.

Neutron fission cross sections in the range of 0.02 - 1.80 MeV have been studied using the Reactor Engineering Division Van de Graaff. Recently Pu^{238}, Pu^{241}, Am^{241} and Am^{243} have been measured.

In addition to the Fast Chopper and the Van de Graaff measurements, effective pile neutron cross sections, both capture and fission, are also being measured. These neutron cross sections are of practical importance. Pu^{243}, Bk^{249}, and Cm^{248} are now being investigated.

Fast Chopper measurements will be made with Cm^{247}, Cm^{248}, Bk^{249}, Cf^{250}, and Cf^{251} when these isotopes are available in sufficient quantities. Effective pile neutron cross sections of some heavy curium isotopes, californium and einsteinium will be measured during the next year.

Publication:

R. E. Cote, R.J. Barnes and H. Diamond, "The Total Neutron Cross Sections of Cm^{244} and Cm^{246}," to be published, Physical Review, 1964.

ARGONNE NATIONAL LABORATORY Chemistry Division

N. Sugarman[*]/S. Mukkergi[*]/K. Weilgoz[*]/J. A. Panontin/
E. P. Steinberg

3/26/64

STUDY OF FISSION-SPALLATION REACTIONS IN HEAVY ELEMENTS

This experiment has been scheduled for the ZGS at Argonne and will be initiated as soon as the machine becomes operational.

The mechanism of fission at high energies will be studied with respect to total kinetic energy release, the excitation energy deposited in the target nucleus by the bombarding proton, and the anisotropy of the process itself. Several targets have been selected of which U^{238} and Bi^{209} would be the first investigated.

Previous studies at lower energies (450 MeV proton fission of U^{238}) indicate that the two wings of the mass-yield fission curve appear to be predominantly formed by two different processes, described as high and low deposition energy events. It is of interest to determine whether the low-energy process is still prevalent at higher bombarding energies and to determine the variation of average deposition energy with incident particle energy. Other mechanisms, such as spallation and "fragmentation" should become more dominant at higher energies, especially for neutron deficient species and very light products.

The observed average excitation energy deposited for the formation of a given product will be compared with the results of Monte Carlo calculations.

The formation ratios and recoil properties of isomeric pairs will also be investigated to obtain information of angular momentum effects in these reactions.

[*] Enrico Fermi Institute, University of Chicago, Chicago, Illinois

ARGONNE NATIONAL LABORATORY

Chemistry Division

E. P. Steinberg/L. Winsberg/J. A. Panontin*/
L. L. Schwartz†

3/26/64

RANGE-ENERGY RELATIONS FOR HEAVY RECOIL FRAGMENTS OF HIGH ENERGY NUCLEAR REACTIONS

The differential recoil cross-sections needed for the interpretation of high energy nuclear reactions have involved the determination of recoil energies and momenta from measured range data. There have been some recent theoretical and experimental studies of range-energy relations, and a renewed interest in this field is apparent. However, there is still considerable uncertainty in the utilization of differential range measurements.

We have carried out a study of the differential ranges of C^{11} fragments in thin aluminum catcher foils over the energy range 3-6 Mev. Recoils of known energy were produced by the reactions $B^{11}(p,n)C^{11}$ and $B^{11}(He,T)C^{11}$ at the ANL Tandem Van de Graaff. These measurements are directly applicable to the ranges observed in the $C^{12}(p,pn)C^{11}$ study reported above. In addition, comparisons with the theory of Lindhard et al. and the work of Northcliffe are being made.

During the next year, we plan to apply time-of-flight techniques to the study of the recoil fragments from high energy nuclear reactions to evaluate, and perhaps avoid, some of the difficulties of range to energy conversion.

---

*University of Chicago, Chicago, Illinois

†Western Reserve University, Cleveland, Ohio

ARGONNE NATIONAL LABORATORY Chemistry Division

E. P. Steinberg/L. Winsberg/J. A. Panontin*/
L. L. Schwartz†

3/26/64

DIFFERENTIAL RECOIL STUDY OF THE $C^{12}(p,pn)C^{11}$ REACTION

A preliminary study of the $C^{12}(p,pn)C^{11}$ reaction was made with the external 450 Mev proton beam of the University of Chicago Synchrocyclotron using a polystyrene target and stacked, thin aluminum catcher foils at 30°, 60°, 90°, 120° and 135° to the beam direction. Although it was possible to obtain reasonably good average range values for the recoils at these angles, the intensity was so low that large catcher foils were necessary. The resulting angular resolution was very poor. In addition, the low intensity prevented any observation of a high-momentum tail on the distributions. The data have been analyzed, therefore, in terms of the experimentally obtained average range.

The results obtained are consistent with the description of the C^{12} and C^{11} ground-state wave functions as pure harmonic-oscillator, single-particle states, with the distortion effects included by leaving the spring constant as a parameter to be determined from the data. The constant so obtained agrees with the value (~ 8 Mev) obtained from nucleon density distributions by electron scattering experiments. This indicates that the distortion effects are small.

However, this result is very preliminary and rather crude. We hope to utilize the high intensity proton beam of the ZGS to obtain data of higher angular resolution and sufficient intensity to examine the high momentum tails of the distribution in detail. These data should then lead to a more meaningful analysis.

*University of Chicago, Chicago, Illinois

†Western Reserve University, Cleveland, Ohio

ARGONNE NATIONAL LABORATORY Chemistry Division

A. Stehney 3/26/64

RADIOCHEMICAL STUDIES OF NUCLEAR REACTIONS RESULTING FROM MUON CAPTURE

Negative muons produced by decay of pions may be absorbed in target materials where they enter into atomic orbitals and are subsequently captured by the nucleus. Most of the work on muon capture has been done by counter techniques in which the emitted particles are observed. The identification and measurement of the reaction products by radiochemical techniques has been difficult because kilogram amounts of target were necessary in order to obtain adequate counting rates. Muon beams of much higher intensity are now available at CERN (Geneva) and, more recently, at the University of Chicago.

In the present work, the use of these high-intensity beams for radiochemical studies is being investigated for application to measurements of the excitation energy imparted to the nucleus after capture, and as a simple analytical technique of measuring the relative frequency of capture of muons by the constituent elements of compounds used as targets. The former is believed to reflect the momentum distribution of protons with the nucleus and the latter may resolve conflicting experimental results as to whether nuclear charge effects extend to the outermost electrons of atoms in insulator type materials.

In cooperation with the nuclear chemistry group at CERN, iodine and zinc targets were irradiated for periods up to 10 hours in the high-intensity muon beam of the CERN synchrocyclotron. Stopping rates of 5×10^5 muons per minute were obtained for targets weighing 500g, and the counting rates of higher-yield products were easily adequate for identification by decay periods. Calibration data are still being obtained and further irradiations are being made by the CERN group.

2A13

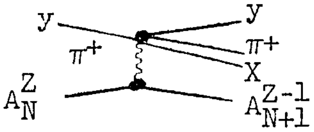
ARGONNE NATIONAL LABORATORY Chemistry Division

E. P. Steinberg/A. F. Stehney/L. Winsberg 3/26/64

THE INVESTIGATION OF $(p,p\pi^+)$ REACTIONS

This experiment has been scheduled for the ZGS at Argonne and will be initiated as soon as the machine becomes operational.

The possibility of obtaining fundamental information from the study of this reaction is indicated by the papers of Chew and Low [Phys. Rev. 113, 1640 (1959)] and T. Ericson *et al.* [Nuclear Physics 36, 353 (1962)]. They have shown how one can relate the differential recoil cross section for the $(y,y\pi^+X)$ reaction on any target nucleus to the free π^+-y total cross section. This relation assumes that the principal contribution to the cross section comes from diagrams of the type where y is any incident bombarding particle and X is a collective line for any further particles which satisfy appropriate conservation laws.



The essential theoretical point is that by measuring the angular and energy distribution of the recoil nucleus A^{Z-1}_{N+1} one can obtain the total π^+-y cross section over a range of energies whose values are related to the energy and momentum of the recoil nucleus. For example, if $y = \pi^+$ or π^- we would have a method of measuring the π^+-π^- or π^+-π^- total cross sections at different energies, cross sections about which almost nothing is known experimentally.

The validity of this method of obtaining such cross sections requires that the effect of many approximations made in the theoretical development be small. As a test of the method, we will first investigate the $(p,p\pi^+X)$ reaction to determine $\sigma_{\pi\text{-}p}(E)$ and compare it with known values.

Bombardments of P^{31}, Cu^{65}, Ag^{109}, Au^{197} and Bi^{209} are planned using the internal proton beam of the ZGS at 6 and 12 Bev. The kinetic energy distribution of recoiling atoms from the $(p,p\pi^+)$ reaction will be measured by a 2π stacked catcher foil technique.

Future work is planned to obtain the angular distribution of the recoils and to study the $(\pi,\pi\pi^+)$ reaction with the ultimate aim of determining the mechanism of simple nuclear reactions and the nature of the π,π interaction.

2A14

ARGONNE NATIONAL LABORATORY Chemistry Division

L. E. Glendenin/H. C. Griffin[*]/K. F. Flynn/
N. Ravindran[†] 3/26/64

FISSION PROCESS STUDIES

Investigation of the relative yields of nuclear isomers by direct formation in fission may shed some light on the question of how much nuclear spin is imparted to the primary fragments in the fission process. Yields for the isomeric pair Te^{131m} (spin 11/2) - Te^{131g} (spin 3/2) were measured in thermal-neutron-induced fission of U^{233}, U^{235}, and Pu^{239}. Preferential formation of the isomer of higher spin may be taken to indicate high nuclear spin in the primary fission fragments. Future studies will include the isomers of Nb^{95} and Pd^{111} for which preliminary evidence points to a preferential formation of the low spin isomer contrary to expectations.

A radiochemical study has been made of the distribution of mass in thermal-neutron-induced fission of Th^{229}. A similar study will be made for Cm^{245}.

In connection with the problem of charge distribution in fission the independent yields of shielded nuclides in the relatively unexplored near-symmetrical mass region are under investigation.

A new program in the study of the fission process now underway is the direct physical determination of the division of nuclear charge (atomic number) as a function of mass split. The experimental technique involves the measurement by a proportional gas counter (or NaI detector) of the energy of the characteristic K x-rays emitted by the excited fission fragments in coincidence with two solid-state fission fragment detectors which determine the mass split by measurement of the fragment kinetic energy ratio. Preliminary experiments with a Cf^{252} spontaneous fission source indicate that the prompt x-rays accompanying fission arise from interval conversion of the γ-rays emitted in the de-excitation of the primary fission fragments, and not from any K vacancies that might be caused by the fission process itself. In the near future this study will include neutron induced fission of U^{233}, U^{235}, and Pu^{239}, but may be expanded later to include charged particle fission.

---

[*] Massachusetts Institute of Technology, Cambridge, Massachusetts

[†] Atomic Energy Establishment, Trombay, Bombay, India

ARGONNE NATIONAL LABORATORY Chemistry Division

J. R. Huizenga/R. Vandenbosch*/J. P. Unik

3/26/64

INVESTIGATION OF THE NEAR-THRESHOLD FISSION OF U^{235} BY MEANS OF THE $U^{234}(d,pf)$ REACTION

The fission of the nucleus U^{235} is being studied near the fission threshold by use of the $U^{234}(d,pf)$ reaction. A three parameter analyzer is used to record the kinetic energies of the proton and both fission fragments for each nuclear event. The energy of the absorbed neutron and hence the excitation energy of the U^{235} nucleus can be calculated from the measured proton energy. The masses of both fission fragments can be calculated from the measured fragment energies. With this information the fission properties of the U^{235} nucleus such as correlations between the total kinetic energy release, fragment mass, nuclear excitation energy, fragment angular distributions, etc. can be simultaneously studied over a wide range (4 MeV) of well defined excitation energies. This work has shown: 1) within the first 2 MeV above threshold, fission proceeds through at least eight groups of nuclear states, 2) at a specific nuclear excitation energy, fission fragments of all masses have the same angular distribution, 3) the average total kinetic energy release varies by less than 0.8% for the different groups of fissioning states observed.

Further experimental work is being planned and theoretical investigations are currently in progress to interpret the various observed fissioning states.

Publication:

R. Vandenbosch, J. P. Unik, J. R. Huizenga and B. D. Wilkins, "Fission Fragment Correlations for the $U^{234}(d,pf)$ Reactions," Bulletin, American Physical Society, Washington Meeting (1964).

---

*Department of Chemistry, University of Washington, Seattle, Washington

2A16

ARGONNE NATIONAL LABORATORY Chemistry Division

L. Winsberg 3/26/64

RECOIL STUDIES OF NUCLEAR REACTIONS INDUCED BY HIGH ENERGY PARTICLES. I. THE PRODUCTION OF Tb^{149}

A paper of the above title has been submitted for publication in the Physical Review. The purpose of this study was to determine as much as possible about the mechanism of proton and alpha-particle induced reactions by the application of relatively simple techniques. The targets employed were Ta, Au, and Bi. The range of proton energies was ~ 0.4 - 6.2 Bev; in the case of alpha particles, 0.5 - 0.88 Bev. The experimental results were then analyzed for the details of the mechanism by applying the laws of energy and momentum conservation in a general way.

This program will be continued with the following objectives:

1. Continue these experiments with protons of energies up to the maximum available at the Argonne ZGS accelerator.

2. Apply the latest modifications of nuclear evaporation theory to the information gained from these experiments in order to determine the role of nuclear evaporation in these reactions.

3. Investigate whether the optical or some other model is useful in interpreting these reactions.

ARGONNE NATIONAL LABORATORY Chemistry Division

J. P. Unik 3/26/64

INVESTIGATIONS OF GAMMA RAYS AND NEUTRONS EMITTED FROM FISSION FRAGMENTS

Investigations are currently in progress to study the gamma rays and neutrons emitted by fission fragments. Using a multiparameter analyzer, correlations are being studied between the fission-fragment masses and the energy spectra and half lives of the gamma rays emitted by the fragments. The spectra of "prompt" gamma rays ($t_{\frac{1}{2}} \leq 10^{-8}$ sec) have been found to be extremely complex and will require elaborate analysis. The gamma rays emitted between 10^{-8} and 10^{-7} sec after fission come from four principal mass groups with average masses of 99, 107, 134, and 146. The study of these gamma-ray spectra for various fragment masses provides information on the energy levels in very neutron excess nuclei that can not be studied by any other means.

An investigation has recently been initiated to study the frequency distribution of neutrons emitted from fission fragments as a function of the fission-fragment mass for nuclei of varying nuclear excitation energy. This study will provide information on how the initial nuclear excitation energy is divided between the two fragments and could possibly determine which of the two current nuclear fission theories (two mode hypothesis or fragment-shell theory) is more accurate.

ARGONNE NATIONAL LABORATORY Chemistry Division

J. E. Gindler/K. Flynn/J. R. Huizenga 3/26/64

FISSION STUDIES

1. The anisotropic distribution of individual fission fragments is of interest because of the correlation between anisotropy and asymmetry. Initial results with 43-MeV alpha-particles on radium show that fission products with a mass ratio of 1.01 to 1.28 have an average W(165°)/W(90°) anisotropy of 1.77. Fission products with a mass ratio of 1.47 to 1.72 have an average anisotropy of 2.26. This study is to be extended to other alpha-particle energies.

2. Fission product mass distributions resulting from the bombardment of Ra^{226} with 10.5 MeV protons are triple-peaked. This is a result of Ac^{227} and Ac^{226} nuclei undergoing fission. Actinium-227 may be prepared by the $Ra^{226}(n,\gamma)\ Ra^{227}\ \beta^- \rightarrow Ac^{227}$ process. It is planned to irradiate Ac^{227} with photons of 11 MeV and to determine the mass distribution of its fission products. Iradiations with 18-MeV photons will result in both Ac^{227} and Ac^{226} fissioning. These mass distributions will be compared with the distributions that have been measured for proton-induced fission of radium. It is expected that other fission measurements will be made with actinium as the target material: anisotropy, cross sections, and kinetic energy distributions of the fission fragments. This will be done for a variety of projectiles: protons, deuterons, and alpha-particles.

ARGONNE NATIONAL LABORATORY Chemistry Division

J. R. Huizenga/J. P. Unik 3/26/64

KINETIC ENERGY CORRELATIONS

Two-dimensional analysis of fission fragment kinetic energies is a powerful method of studying mass distributions and kinetic energy distributions. A series of experiments has been completed for the fissioning nuclei produced by bombardment of Bi^{209}, Ra^{226}, and U^{238} with 30 to 42 MeV helium ions. A large amount of structure in the mass and energy correlations has been observed in the case of Ra^{226} and to a lesser extent in the case of U^{238}. The maximum total kinetic energy release in the case of Ra^{226} and U^{238} fission occurs at $M_H = 135$, while a maximum in the variance of the total kinetic energy occurs at $M_H = 131$. This structure in the kinetic energy is interpreted in terms of shell structure in the heavy fragment.

The full width at half maximum height in the total kinetic energy distribution for 42-MeV helium-ion-induced fission of Bi^{209} is 16 ± 1 MeV in excellent agreement with a theoretical calculation of Swiatecki and Nix.

A full report on the details of these experiments has been accepted for publication in the Physical Review. Present and future correlations of the fission fragment kinetic energies are to be done with at least one additional parameter.

<u>Publication:</u>

J. P. Unik and J. R. Huizenga, "Binary Fission Studies of Helium-Ion-Induced Fission of Bi^{209} and U^{238}," in press, Physical Review, April (1964).

ARGONNE NATIONAL LABORATORY Chemistry Division

P. R. Fields/A. M. Friedman/H. Diamond 3/26/64

FISSION PROPERTIES OF THE ACTINIDE ELEMENTS

The distribution of the kinetic energy of fission fragments have been measured for a great number of nuclides using neutron induced fission and spontaneous fission. $\bar{\nu}$ (number of neutrons emitted per fission) as a function of mass split, delayed neutron groups, long range alphas, gamma rays, and the distortion of fission fragments in fission are also investigated. In some cases these parameters are measured at different neutron energies. Various coincidence techniques, detectors, multichannel and multiparameter analyzers have to be employed in the program. One of the most recent studies involves searching for tripartite fission where the three fission fragments are roughly of equal mass and measuring the frequency and the total energy of such fission events. Cf^{252} spontaneous fission and neutron induced fission of U^{235} are being investigated for tripartite fission.

The fission characteristics of Cf^{252} have been and still are being measured in preparation for using this isotope as a primary neutron standard.

Fission fragment distortion in U^{235} fission at various neutron energies will be studied as well as the fission characteristics of Cm^{248}, Fm^{254} and Fm^{256}.

Publications:

A. M. Friedman, J. W. Meadows, A. B. Smith, P. R. Fields, J. Milsted and J. F. Whalen, "Fission Fragment Kinetic Energies of Cf^{246}, Cf^{248} and Cf^{254}," Phys. Rev. 131, 1203 (1963).

P. R. Fields and H. Diamond, "Cf^{252}: A Primary Standard for Neutrons; Neutron Dosimetry," Vol. II, IAEA, Vienna, 581 (1963).

2A21

ARGONNE NATIONAL LABORATORY Chemistry Division

L. E. Glendenin/K. F. Flynn/A. Jaffey 3/26/64

HALF-LIVES AND DECAY SCHEMES

Considerable effort is being devoted to a study of the natural radioactivities of importance in geochemistry since accurate decay constants for K^{40}, Rb^{87}, Th^{232}, U^{235}, and U^{238} are needed in the geochronology of rock systems. Accurate measurements of the half-lives of K^{40}, Rb^{87}, and Th^{232} and a study of the decay scheme of K^{40} are essentially completed, and determination of the half-lives of U^{235} and U^{238} are in progress.

Also under investigation are the half-life and β^- spectrum of the naturally occurring radionuclide Lu^{176} and the half-lives of the fission products Pd^{107}($\sim 10^7$ years) and Sm^{151} ($\sim$ 100 years). Future studies will include natural radioactivities such as In^{115} and Ac^{227} and the fission products Se^{79} ($\sim 10^5$ years, forbidden β^- spectrum) and I^{129} (10^7 years, forbidden β^- spectrum).

Publications:

L. E. Glendenin, "Present Status of the Decay Constants," Annals. of the New York Academy of Sciences 91, 166 (1961).

D. W. Engelkemeir, K. F. Flynn, and L. E. Glendenin, "Positron Emission in the Decay of K^{40}," Phys. Rev. 126, 1818 (1962).

ARGONNE NATIONAL LABORATORY Chemistry Division

J. Gindler/D. W. Engelkemeir/M. S. Freedman, et al./
F. S. Tomkins, et al. 3/26/64

NUCLEAR DECAY SCHEMES

The long-lived Np^{236} isomer has been prepared by the U^{235}(d,xn)Np^{237-x} and U^{238}(d,xn) Np^{240-x} reactions. Neptunium from the first reaction was separated into its various mass components. In the 236 mass a very low intensity gamma-ray with an energy of 162 kev was observed. Coincidence measurements showed this gamma-ray to be in coincidence with K- and L-X-rays. This same gamma-ray was observed in the neptunium formed by the deuteron bombardment of U^{238}. However, so little neptunium was formed in this reaction that no mass spearation was attempted. Consequently, Np^{237} and its Pa^{233} daughter contributed radiations that interfered with the determination of the Np^{236} decay scheme. A larger amount of neptunium has been prepared by the U^{238} (d,xn) reaction. It is anticipated that separation of the various neptunium masses will be possible and that a clearer understanding of the long-lived Np^{236} decay will result.

The decay of Th^{229}, initiated by alpha and gamma-ray measurements, has been continued. Conversion electron spectra have been studied using the double beta coincidence spectrometer. The conversion electron spectrum has been studied both in single operation and in coincidence with selected alpha groups. These studies are being continued with improved resolution.

Further studies of the optical hyperfine structure of Th^{229} are planned. Previous measurements with the 30 foot grating spectrograph have given five components of selected emission lines. This indicates that the nuclear spin of Th^{229} is greater than 3/2 and is probably 5/2. A more definitive spin determination is expected with a new grating of higher resolving power.

2A23

ARGONNE NATIONAL LABORATORY Chemistry Division

M. S. Freedman/F. T. Porter/F. Wagner, Jr. 3/26/64

BETA RAY SPECTROMETRY

The general program of decay scheme analysis on the Double Electron Coincidence Spectrometer, particularly in the heavy elements, has been started with Th^{229} and Cm^{241}. Conversion electron and alpha-electron coincidence studies on these complex schemes demonstrated the need for electron-electron coincidence measurements, particularly at energies as low as a few Kev.

To this end, substantial effort has been invested in the development of efficient low energy electron scintillation detectors. One result of this work is the first measurement of the specific scintillation response of NaI·Tl to electrons as a function of electron energy, in good agreement with semi-empirical theoretical predictions. Similar measurements were made in anthracene and scintillating plastic, together with measurements of the intensity and lifetimes of numerous delayed scintillating states in all three scintillators. We now have detectors with usable efficiency as low as one Kev, and high, but not yet accurately known efficiency at 5 Kev.

In addition to the program of decay scheme studies, we plan three investigations in the near future: the continuous spectrum of internal conversion electrons (inner bremsstrahlung conversion) accompanying electron capture, in Fe^{55} (an intense, pure source must be obtained for this experiment); a detailed study of the shape of the beta spectrum of tritium near its endpoint, with reference to the problem of the mass of the antineutrino; and a strong effort to improve the absolute accuracy of spectrum shape determinations, to redress the gross discrepancies in these difficult, sensitive experiments between the results of various investigators.

Publication:

M. S. Freedman, F. T. Porter, I. Sherman and F. Wagner, Jr. Proc. IRE 9th Scint. Counter Symposium. "Electron response of NaI·Tl and a comparison with anthracene and Pilot B."

ARGONNE NATIONAL LABORATORY Chemistry Division

P. Day 3/26/64

COMPUTER ANALYSIS OF BETA SPECTRA

The determination of the electron distribution involved in a nuclear beta-decay requires a considerable amount of routine computation. In order to relieve the experimenter from these routine calculations and eliminate the possibility of making arithmetical errors, a computer program is being written in FORTRAN to process the experimental data. All data points are corrected for background and decay, then the average of all measurements at each spectrometer setting along with the standard deviations are calculated. A resolution correction is then made using the first and second moments of the spectrometer line shape. This is accomplished by finding the first and second derivatives of the momentum plot obtained by fitting groups of five points with a second order polynomial using a weighted least square method. The energies are calculated from the spectrometer calibration constant, and then the screening corrected values of the Fermi function are obtained from a stored table using the LaGrange method of three-point interpolation. A weighted linear least square analysis is then run yielding the beta spectrum end-point and area with their standard deviation. Finally the data for a "shape plot" with standard deviations is produced. There will be several options in analyzing a particular experiment. Various kinds of backgrounds including other beta spectra may be subtracted at appropriate phases of the computation. It will also be able to compute theoretical "shape factors" by various methods and apply these to the beta spectrum before the weighted linear least square analysis of the spectrum is made. A measure on the usefulness of such a program can be obtained by noting that a similar program written several years ago for the IBM-650 computer took about 15 minutes to process 500 spectrometer settings, whereas desk calculator processing required about 3 days.

ARGONNE NATIONAL LABORATORY Chemistry Division

P. Day/R. Steffen[*] 3/26/64

BETA-SPECTRAL SHAPE OF THE Sb^{122} DECAY

Recently there have been various attempts to explain the relative sizes of the nuclear matrix elements involved in first forbidden non-unique beta transitions. Such concepts as "K-forbiddeness" and "j-forbiddeness" have not been fully successful in explaining the relative sizes of the matrix elements deduced from the experimental data. All or part of this discrepancy may be due to inadequate experimental data. Measuring the "shape" of the electron distribution in a beta-decay process is one of the experimental techniques used for determining the relative sizes of the matrix elements. Another useful technique is to measure the beta-gamma circular polarization and the beta-gamma angular correlation.

Dr. Rolf Steffen is currently measuring the beta-gamma circular polarization and beta-gamma angular correlations involved in the beta-decay of Sb^{122}. These measurements indicate that there is a considerable contribution from the B_{ij} nuclear matrix element involved in the beta-transition to the second 2+ state, but little contribution from this matrix element in the beta-transition to the first 2+ state. Currently accepted theoretical considerations indicate that both of these 2+ levels may be characterized as vibrational states. It is thus not clear why there should be a difference in the relative sizes of the nuclear matrix elements involved in the two transitions.

In order to further determine the relative contributions of the nuclear matrix elements involved in the two transitions, the shape of the electron distribution to each of the excited states will be measured in coincidence with its appropriate gamma-ray on the Argonne double-lens beta-spectrometer.

The "shape" measurements, along with the results of the angular correlation measurements will permit a careful evaluation of the relative contributions of the six nuclear matrix elements that are involved in these two first-forbidden non-unique beta-transitions. If indeed it turns out that the two transitions are different in character, it will either mean that the current ideas regarding the nature of even nuclei level structure are inadequate or else there is a yet unknown selection rule operating in nuclear beta-decay.

[*] Physics Department, Purdue University, LaFayette, Indiana

ARGONNE NATIONAL LABORATORY Chemistry Division

D. L. Horrocks 3/26/64

LIQUID SCINTILLATOR STUDIES

Work has been completed on the liquid scintillator studies of alpha particle energy resolution, average energy required to produce one photoelectron and pulse height-energy relationship for low energy electrons. Also completed is the study of fission fragment interaction with organic scintillators.

Further studies are planned on other applications of liquid scintillators, i.e., quenching measurements, half-life measurements, spontaneous fission determination.

Other work has been concerned with detection of tritium produced during fission. The amount of tritium produced during fission of other fissionable isotopes will be pursued.

Publications:

D. L. Horrocks, "Alpha Particle Energy Resolution in a Liquid Scintillator," Rev. Sci. Instr. 35, 334 (1964).

D. L. Horrocks, "Liquid Scintillator - Methods for Calculation of Average Energy Required to Produce one Photoelectron," Nucl. Instr. and Methods 24, 0000(1964) in press.

D. L. Horrocks, "Interaction of Fission Fragments with Organic Scintillators," Rev. Sci. Instr. 34, 1035 (1963).

D. L. Horrocks, "Tritium Produced during Spontaneous Fission of Californium-252," Phys. Rev. in press (1964).

ARGONNE NATIONAL LABORATORY Chemistry Division

C. Stevens/P. Moreland/K. Kaiser 3/26/64

NUCLEAR CHEMISTRY

Analysis of the abundance of uranium-236 in natural uranium is being carried out using a combination of electromagnetic isotope separation and the Argonne 100-inch mass spectrometer. Two measurements so far give a concentration between 3-6 x 10^{-10}.

Future plans involve work in several areas. Preparation of an instrument for precision measurements of nuclidic masses has been continuing. Plans call for measurements of secondary mass standards (C-12, O-16, H, D, S-32); electron-capture radioactive nuclides where nuclear reaction measurements have poor accuracy; and other regions of the periodic table of special interest.

Experiments are planned aimed at high sensitivity analysis. These involve identification and half-life of Mn-53, half-life of Si-32, and search for possible long-lived nuclides Ca-40, Au-199, and Au-200.

Plans have been made to study the structure of high molecular weight organic compounds.

A two-stage mass spectrometer which has been under construction for several years will be completed in the coming year. This instrument will be used for investigations of very small concentrations of long-lived isotopes either produced in nuclear reactions or occurring naturally.

An extensive study of the isotopic and elemental abundance of the silver isotopes in seven meteorites was completed and published. An enrichment of Ag^{107} would indicate the occurrence in the meteorite at the time of solidification of the now extinct radioactive nuclide Pd^{107} ($T_{\frac{1}{2}} = 7 \times 10^6$ y), and therefore perhaps provide a means of studying presolidification history of the solar system. The results of an extensive study involving many accurate analyses of seven meteorites showed no significant difference between meteoritic and terrestrial silver, which contradicts an anomaly reported by another laboratory.

Publication:

A. Chakraburtty, C. M. Stevens, E. Anders and H. Rushing, "Isotopic Composition of Silver in Iron Meteorites," J. of Geophy. Res. 69, No. 3, 505 (1964).

2A28

ARGONNE NATIONAL LABORATORY Chemistry Division

A. Turkevich*/J. H. Patterson 3/26/64

LIGHT ELEMENT ANALYSIS BY RUTHERFORD SCATTERING

The instrument devised for the analysis of the lunar surface by means of alpha scattering has now been accepted by NASA for inclusion in the Surveyor instrument-landing program. This system, which is to be deployed from the spacecraft by an arm to make in situ surface measurements, also uses the proton spectrum from the (α,p) nuclear reaction of some of the lighter elements to improve the resolution and accuracy of the analysis from the alpha scattering.

Future work will involve further refinement of the method and improvement of the instrumentation, as well as testing of the equipment for reliability after exposure to flight and lunar environmental conditions. High-level curium-242 sources must also be prepared at ANL for the instruments to be used for research and testing, as well as periodic replacement of sources in the instruments now in use.

This program is being carried out in cooperation with Professor A. Turkevich, Consultant, University of Chicago, and Mr. Ernest Franzgrote of Jet Propulsion Laboratory.

---

*University of Chicago, Chicago, Illinois

ARGONNE NATIONAL LABORATORY Chemistry Division

G. W. Reed, Jr./A. L. Turkevich[*] 3/26/64

GEO-COSMOCHEMISTRY

The problem of trace element content and isotopic composition of meteoritic matter is being studied using, primarily, activation techniques. The information gained will be useful in understanding the nucleogenesis of solar system matter, the possible nuclear, physical and chemical processes to which this material has been subjected, and the time sequence of these phenomena.

Specific areas under investigation are: (1) the amounts and distribution of the trace anionic species, halogens in particular. Here photonuclear neutron and charged particle activations are or will be used; (2) the concentration and isotopic composition of Pb -- charged particle analyses will permit the determination of at least 3 of the isotopes. Previous work using fast and slow neutrons has demonstrated the feasibility of such an approach, and there is a critical need for measurements independent of use of the mass spectrometer; (3) the determination of the concentrations and distribution of the heavy elements will continue.

<u>Publications</u>:

G. Reed, "Heavy Elements in the Pantar Meteorite," J. Geophys. Res. 68, 3531 (1963).

G. Reed, "Fluorine in Stone Meteorites," Geochim. et Cosmochim. Acta (in press) (1964).

[*] University of Chicago, Chicago, Illinois

2A30

ARGONNE NATIONAL LABORATORY Chemistry Division

L. Fuchs/K. Jensen 3/26/64

MINERALOGICAL AND CHEMICAL ANALYSES OF METEORITES

The chemical and mineralogical analyses of the polymict brecciated Plainview, Texas meteorite have been completed. The results are to be presented before the meeting of the American Geophysical Union, April 24, 1964. Serious discrepancies were found in the metallic iron, sulfur, and phosphorus results published in the literature. Values for previously unreported titanium, copper, carbon, and water were determined. The presence in this meteorite of tridymite and cristobalite restricts the maximum pressure to four kilobars since the formation of these minerals. Some problems encountered in this study will receive additional attention in the continuing program. One of these is concerned with the assignment of phosphorus to specific minerals. Only one-fourth of the phosphorus content of the Plainview meteorite resides in the phosphate mineral whitlockite. Using a neutron activation analysis technique, it was found that less than one percent of the phosphorus is present in the metal phase. The site of the remaining phosphorus will be determined by an electron microprobe when one becomes available. The distribution of this element, together with a knowledge of its oxidation state, will provide important information on the conditions of formation of stony meteorites.

Publication:

L. H. Fuchs, "Occurrence of Whitlockite in Chondritic Meteorites," Science, 37, 425 (1962).

2A31

ARGONNE NATIONAL LABORATORY Chemistry Division

D. C. Stewart/M. A. Wahlgren 3/26/64

SEARCH FOR ELEMENT 61 IN NATURE

Small traces of element 61 (promethium) might be present in natural materials, either as an undiscovered long-lived isomer, as the daughter of a long-lived isomer of neodymium or samarium, or from spontaneous fission of uranium. As starting material for a search for promethium in nature, a two hundred pound rare earth concentrate representing 17,500 pounds of rare earth ore was purchased from a commercial supplier.

This concentrate consisted of the neodymium-samarium interface from the supplier's four-foot diameter rare earth production ion exchange column. Any promethium, if present, would be expected to concentrate at this interface. To concentrate the promethium further, a series of smaller scale ion exchange column runs has been made, with the samarium-neodymium interface fraction of each run being used as feed for the next column in succession. The cycling process has been carried out to the point where gram amounts of Nd-Sm are involved.

As time permits, concentration will be continued until the final "promethium" concentrate can be analyzed for element 61 by counting methods, spectrographic analysis, mass spectrometry, etc.

ARGONNE NATIONAL LABORATORY Chemistry Division

H. H. Strain/H. D. Frame 3/26/64

ANALYSIS BY DIFFERENTIAL MIGRATION

The separation of mixtures and the isolation of the components are essential steps in the investigation of chemical substances. Two of the most effective methods for these separations are chromatography and electrochromatography. Numerous studies of both these differential migration methods have already been reported.

Our current investigations of chromatography and electrochromatography fall into two principal categories; namely, fundamental studies and special applications. In chromatography, the basic studies include the selection of chromatographic systems and the definition of the adsorptive and solution forces. In electrochromatography, the basic investigations show that complex formation is critical in the separation of the cations.

In the area of special applications, adsorption chromatography is serving for the isolation of ordinary chlorophylls, fully deuteriated chlorophylls from various plants, and isomerization and pyrolysis products of the chlorophylls. These methods have been utilized to examine the chloroplast pigments of about 200 Australian plants growing under a variety of environmental conditions. Electrochromatography is being used for the separation and isolation of various radioactive species. These separations have been made over a wide range of concentration, including the lowest detectable concentration.

Many new applications, prerequisite to progress in other problems, are under investigation. Examples are the role of chlorophyll in photosynthesis and the detection of trace elements following neutron activation.

Publications:

J. Sherma, G. H. Evans, H. D. Frame and H. H. Strain, "Separation of Certain Metal Ions from Mixtures by Electrochromatography," Anal. Chem. 35, 224 (1963).

C. K. Miller, D. Steffenson, H. D. Frame and H. H. Strain, "Activated Cellulose for Solution-Adsorption Chromatography," Anal. Chem. 35, 93 (1963).

Chlorophyll Investigations: J. Am. Chem. Soc. 85, 4049 (1963).

2A33

ARGONNE NATIONAL LABORATORY Chemistry Division

D. C. Stewart/M. A. Wahlgren/W. C. Mohr 3/26/64

ISOTOPIC SOURCE NEUTRON FACILITY

Current production plans call for gram quantities of Cf^{252} to be available within a few years. One gram of Cf^{252} emits about 3 x 10^{12} neutrons/second from spontaneous fission, offering a neutron flux roughly equal to that of a small reactor. Unlike a reactor the Cf^{252} source does not vary unpredictably in output, is not subject to frequent shutdown, has an invariant neutron spectrum, and would be relatively accessible for incorporation of a wide variety of experimental facilities. An irradiation facility based on Cf^{252} neutrons therefore would have many uses in research and in analysis by activation methods.

A prototype facility using Cm^{242}-Be is currently being designed to afford interim evaluation of the system prior to the availability of Cf^{252}. Twelve Am^{241}-Be sources are being prepared for pile irradiation to convert about one-quarter of the Am^{241} to high specific activity Cm^{242}. The resultant slugs would contain about 0.4 g of Cm^{242} total for a neutron output of about 10^{10} neutrons/second by the (α,n) reaction on beryllium. The Cm^{242}-Be source will be set up in a shielded cell in the new Argonne Chemistry Research Hot Laboratory, with provision for the use of moderators, converters, rabbit tubes, cryogenic equipment, etc. Neutron absorption and scattering; fission fragment, delayed neutron and capture counting; cold, thermal, and fast neutron activation; neutron imaging; neutron radiation effects and empirical testing of neutron shields are among the studies and uses being planned for the facility.

ARGONNE NATIONAL LABORATORY Chemistry Division

M. A. Wahlgren/J. Wing 3/26/64

NON-DESTRUCTIVE ACTIVATION ANALYSIS

For a number of samples in the past it has been possible to eliminate or in some cases to simplify radiochemical separations in activation analysis by utilizing gamma-gamma coincidence with a fast-slow coincidence unit coupled to the multichannel analyzer. In other cases coincidence counting gives a more rapid and unequivocal identification of gamma spectra components than half-life measurements. Equipment at Argonne is accordingly currently being modified to allow sum coincidence counting with the fast coincidence system as an alternate mode.

A table based on Koch's Activation Handbook sensitivities is being prepared to show the calculated sensitivities which can be attained using the coincidence methods in a standard crystal configuration. Where gamma ray abundance data is not available, the sensitivity will be determined empirically. In some cases, as many as three isotopes can be measured simultaneously, and the output data can be punched out on paper tape for computer processing if large numbers of similar samples are to be analyzed.

ARGONNE NATIONAL LABORATORY Chemistry Division

J. Faris/E. Huff 3/26/64

EMISSION SPECTROGRAPHIC ANALYSIS

A program for the reliable detection by spectrographic methods of trace impurities in various materials will be continued. This includes direct methods for the analysis of tungsten in particular, and also for niobium and tantalum. Emphasis will be placed on developing concentration procedures for isolating trace elements for spectrographic determination. Included will be separation of impurities from plutonium bearing alloys and compounds by anion exchange and column extraction.

Publications:

J. P. Faris, "Applications of the Copper Spark Method for Spectrographic Analysis," 6th Conf. on Anal. Chem. in Nuclear Reactor Technology, Gatlinburg, Tenn., AEC Rept. TID-7655, p. 193 (1962).

J. P. Faris and R. F. Buchanan, "Anion Exchange Characteristics of the Elements in Nitric Acid and Nitrate Solutions and Application in Trace Element Analysis," AEC Rept. ANL-6811 (1963).

2A36

ARGONNE NATIONAL LABORATORY　Chemistry Division

B. D. Holt　3/26/64

DEVELOPMENT OF OXYGEN ANALYSIS METHODS

Efforts are being made to extend carbon-reduction techniques (using induction heating) to the direct determination of oxygen in such difficultly analyzed materials as (1) organic phosphates, (2) metals with boiling points points in the 1400°C range, (3) alkaline earth metal oxides, and (4) irradiated refractory metals containing plutonium contamination. The chief difficulties to be overcome are the high sample volatilities in (1) and (2), the gettering of carbon monoxide and the attack on fused silica equipment by freshly-produced magnesium and calcium in (3), and adequate shielding and protective isolation of samples during the extraction and handling of gases in (4).

Previously developed methods are now in use for the determination of oxygen in low boiling point metals (Zn, Cd, Mg) and in various oxides other than MgO and CaO.

Publications:

B. D. Holt and J. E. Stoessel, "Macro Determination of Oxygen in Metal Oxides by Inert Gas Fusion," Anal. Chem., May (1964).

B. D. Holt and H. Goodspeed, "Determination of Oxygen in Zinc, Cadmium, and Magnesium by Carbon-Reduction in an Inert Gas Stream," Anal. Chem. 34, 374 (1962).

ARGONNE NATIONAL LABORATORY Chemistry Division

J. A. Goleb 3/26/64

URANIUM ISOTOPE INVESTIGATIONS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Many elements have been determined analytically in the past by atomic absorption spectrophotometry, but no work has been reported for uranium. The apparent reasons are the general weakness of the lines in the complex spectrum of uranium and the fact that its compounds are not readily dissociated in the flames normally used as absorption sources.

A sputtering technique is currently being developed for the isotopic analysis of masses 235 and 238 in uranium, using water-cooled hollow-cathode discharge tubes. Two emission tubes, one containing a metallic uranium electrode of mass 235; the other, a similar electrode of mass 238, are used to provide resonance radiation which is passed through the sample being investigated. This sample is in the form of a uranium metal cylinder 1 1/2 inches long and of 1/4 inch inside diameter, placed in an absorption tube. When the discharge is started in the absorption tube, microgram quantities of uranium are sputtered and volatilized into the tube cavity and some of the uranium-235 and uranium-238 incident radiation passing through this discharge tube cavity is absorbed in the vapor. The amount of absorption that is measured at selected wavelengths is dependent on the number of ground state uranium-235 and uranium-238 atoms in the light path of the absorption tube. The results obtained to date using this atomic absorption technique on a depleted uranium sample having approximately 0.2% uranium-235 without the use of standard samples are in good agreement with mass spectrographic isotopic results. Further development of the method for application to other uranium compositions will be continued.

The advantage of this atomic absorption technique is that inexpensive instruments are used, in contrast with emission and mass spectrographic methods employing expensive and sophisticated instruments.

Publication:

J. A. Goleb, "Uranium Isotope Investigations by Atomic Absorption," Anal. Chem. 35, 1978 (1963).

ARGONNE NATIONAL LABORATORY
Chemistry Division

S. Wexler

3/26/64

INELASTIC COLLISION PROCESSES OF MeV IONS

Properties of the collisions with isolated molecules of ions with energies in the MeV region have been investigated by means of a portable mass spectrometer with special constructional features. The apparatus was built on a frame provided with casters and jacks so that it can readily be moved into position and aligned with the beam of high-energy ions from any of the several electrostatic ion accelerators at Argonne National Laboratory.

As the initial study of this program, the partial cross sections were determined for the formation of noble gas ions in their various charge states as a result of impact of protons in the range from 0.8 to 3.75 MeV. In addition, an experimental assessment was obtained of the validity of the Born approximation as it applied to molecular ionization and fragmentation. The fragmentation patterns of five lower hydrocarbons resulting from impact of 2.25 MeV protons were compared with those produced by 1225 electrons (the velocities of both projectiles were 2×10^9 cm/sec.)

Study of ion-molecule reactions in gases near one atmosphere pressure is planned. Such investigations with the mass spectrometer attached to an ionizing source of high-energy protons should reveal ionic mechanisms involved in conventional radiation-chemical experiments on gases, particularly of ionic polymerization. An attempt will be made to determine indirectly lifetimes of parent ions against dissociation.

Publication:

S. Wexler and D. C. Hess, "Ionization by Ions in the MeV Range," J. Chem. Phys. 38, 2309 (1963).

2A39

ARGONNE NATIONAL LABORATORY Chemistry Division

S. Wexler 3/26/64

CROSSED-BEAM STUDIES OF REACTIONS OF ACCELERATED ATOMS WITH MOLECULES

In a new approach to the study of the reactions of energetic recoil atoms in "hot atom" chemistry, an apparatus is being designed to observe the chemical behavior of artificially produced hot atoms. An accelerated, collimated and modulated beam of neutral atoms, of well-defined energy varying between 1 and 100 eV, will impinge on a collimated beam of thermal organic or inorganic molecules which intersect the atomic beam at right angles. The products of the reacting beams will be condensed on a cold surface and later subjected to gas chromatographic separation. Identification of the products will be made by measurement of the radioactivity in the separated fractions (if the atomic beam is composed of active nuclides) or by mass spectrometric analysis. In situ mass spectrometric detection will permit measurements of the kinetic energy and angular distributions of the products, as well as offer an alternative method for their identification.

Measurement of the yields of the various reaction products as a function of the kinetic energy of the artificially accelerated hot atom will give the first direct determination of the threshold energies for these endoergic reactions. The observed product distributions will be compared with those obtained in conventional hot atom studies through the use of recoils from nuclear transformations.

2A40

ARGONNE NATIONAL LABORATORY Chemistry Division

W. G. Brown 3/26/64

ORGANIC SOLID STATE RADIATION CHEMISTRY

This work has as its objective the detection and mechanistic interpretation of difference in products and yields in radiation-induced reactions of organic materials in the solid state where such differences can be correlated with the geometry of the molecule or its environment. Included are studies on typical pairs of geometrical isomers to be carried out where possible on liquid, glassy, and pure crystalline state; related studies involve similar pairs in solid solutions and in heterogeneous crystal matrices. Where feasible, parallel studies of gamma ray and ultraviolet irradiation are performed. The specific cases emerging from a preliminary study as worthy of more detailed investigation are cis- and trans-stilbene, cis- and trans- -phenylcinnamic acid, and cis- and trans-1, 2-diphenylcyclopropane. An eventual extension to enantiomorphic pairs is anticipated.

2A41

ARGONNE NATIONAL LABORATORY Chemistry Division

L. M. Dorfman/M. C. Sauer/
I. A. Taub[*]/S. Arai[†]

3/26/64

THE SOLVATED ELECTRON AND MOLECULAR IONS IN POLAR ORGANIC LIQUIDS

By means of the pulse radiolysis technique it has been shown that solvated electrons are formed in the radiation chemistry of the aliphatic alcohols. Some of the physical and chemical properties of this primary radiation chemical species have been investigated in ethanol and methanol.

The absorption spectrum of the solvated electron in ethanol has a maximum at 700 mμ and a shoulder at 520 mμ. The molar extinction coefficient was determined to be $\epsilon^{5461}_{e^-_{sol}} = 1.1 \times 10^4 M^{-1} cm^{-1}$ at 5461 Å, from which the oscillator strength of the overall band was estimated as $f = 0.7$. The G-value for the solvated electron in ethanol is approximately 1.

Absolute rate constants in both ethanol and methanol have been determined for $e^-_{sol} + H^+$, $e^-_{sol} + C_6H_5CH_2Cl$ and $e^-_{sol} + (C_6H_5)_3COH$. The rate constants for the first two reactions are very nearly identical with the analogous constants for the hydrated electron.

In the aliphatic alcohols containing aromatic solutes such as diphenyl, anthracene and terphenyl, the solvated electron becomes attached to form the mononegative ions. These observations establish the role of molecular ions in the chemical stage of liquid phase radiolysis. The anions undergo a proton transfer reaction with the alcohols.

These investigations are being extended to other polar organic liquids.

Publications:

L. M. Dorfman, "Pulse Radiolysis: Fast Reaction in Radiation Chemistry," Science, 141, No. 3580, 493 (1963).

I. A. Taub, M. C. Sauer and L. M. Dorfman, "Pulse Radiolysis Studies of the Reactivity of the Solvated Electron in Ethanol and Methanol," Discussions of the Faraday Society, No. 36 (1963).

---

[*] University of Minnesota, Minneapolis, Minnesota

[†] Tokyo Institute of Technology, Tokyo, Japan

ARGONNE NATIONAL LABORATORY Chemistry Division

E. J. Hart/M. Anbar*/H. Fricke/
S. Gordon/J. K. Thomas

3/26/64

REACTIONS OF THE HYDRATED ELECTRON AND THE HYDROXYL RADICAL

The precursors of hydrated electrons (e^-_{aq}) and hydroxyl radicals (OH), the thermalized electron (e^-) and ionized water molecule (H_2O^+) respectively, are of too short lifetime ($\sim 10^{-11}$ sec) to study. However, notable progress has been made in pulse radiolysis research on rate constants of e^-_{aq} and OH free radical reactions. The use of the transient absorption spectrum of e^-_{aq} greatly facilitates the study of its reactions and rate constants. This simplest and most reactive of all negative ions has a lifetime of some 20 μsec and an intense absorption maximum at 7200 Å. Utilizing this absorption band, the absolute rate constants of about 150 inorganic ions and organic molecules with e^-_{aq} have been obtained. Further work in this area is projected with the purpose of correlating structure and chemical properties of solutes with their e^-_{aq} rate constants. A similar program is under way on the measurements of OH rate constants but progress is slower because the OH absorption band has not been discovered yet in irradiated water. In the meantime, OH rate constants relative to the reaction; $OH + I^- \rightarrow OH^- + I$ followed by $I + I^- \rightarrow I_2^-$, can be made by measuring the relative intensity of the I_2^- absorption maximum as a function of scavenger concentration. An alternative way to obtain H-atom and OH radical rate constants is to use a combination of pulsed and steady electron beam irradiation techniques. This method, requiring kinetic studies, provides an effective tool for getting rate constants of non-absorbing species. Consequently, it supplements the optical absorption method. Continuing effort will be made to obtain reaction rate constants of these primary species and to use them in diffusion kinetic calculations.

Publications:

J. K. Thomas, S. Gordon and E. J. Hart, "The Rates of Reaction of the Hydrated Electron in Aqueous Inorganic Solutions," J. Phys. Chem. (In press).

E. J. Hart, S. Gordon and J. K. Thomas, "A Review of the Radiation Chemistry of Single Carbon Compounds and Some Reactions of the Hydrated Electron in Aqueous Solutions." Radiation Research Supplement, 4, 74 (1964).

H. Fricke and J. K. Thomas, "Pulsed Electron Beam Kinetics," Radiation Research Supplement, 4, 35 (1964).

---

*Weizmann Institute, Rehovoth, Israel

ARGONNE NATIONAL LABORATORY Chemistry Division

E. J. Hart/M. Anbar*/S. Gordon/J. K. Thomas 3/26/64

SPECTRA OF RADIATION INDUCED TRANSIENT SPECIES IN AQUEOUS SOLUTIONS

Pulse radiolysis techniques offer excellent means for studying the properties of intermediate species. Frequently the identification of these species will provide valuable clues to the mechanism of the reaction. And while kinetic data are indispensable in deducing mechanisms, an absorbing intermediate that can be identified and studied is of considerable use too. For example, much success in explaining the fundamental reactions in irradiated water has resulted from the use of the hydrated electron band.

The hydrated electron forms absorbing negative ions of many organic compounds. In these cases, a parent-daughter relationship exists between the decay of the e^-_{aq} absorption band and the formation of the negative ion band. Transient spectra, possibly due to e^-_{aq}, form also in dilute solutions of Zn^{++}, Cd^{++} and Pb^{++} among the inorganic ions and in aqueous phthalic acid, picric acid, thymine, cytosine and acrylamide solutions. Subsequent decay of the transient may be by a second order process (bimolecular recombination) or by a first order process, (Protonization or reaction with water). Not only is the lifetime of the band affected by solutes but the structure of the band is altered by the ionic environment of the solution. The shift in maximum of the e^-_{aq} absorption from 7200 Å to 6000 Å in saturated potassium fluoride or lithium chloride solutions indicates the conversion of e^-_{aq} to a new form, possibly an association with the positive ion. Work will continue on the effect of ionic environment on the structure and reactivity of e^-_{aq} and on the utilization of transient spectra for the interpretation of reaction mechanisms.

Publications:

E. J. Hart and J. W. Boag, "Absorption Spectrum of the Hydrated Electron in Water and in Aqueous Solutions," J. Am. Chem. Soc. 84, 4090 (1962).

S. Gordon, E. J. Hart and J. K. Thomas, "The Ultraviolet Spectra of Transients Produced in the Radiolysis of Aqueous Solutions," J. Phys. Chem., In Press.

E. J. Hart, "Hydrated Electron: Most Reactive and Elementary of all Negative Ions," Science, In Press.

---

*Weizmann Institute, Rehovoth, Israel

2A44

ARGONNE NATIONAL LABORATORY Chemistry Division

M. S. Matheson/J. Rabani[*] 3/26/64

RADIATION CHEMISTRY - PULSED RADIOLYSIS

Pulsed radiolysis research has been carried out during the past year on three systems:

(a) The alkaline aqueous solution saturated with H_2 at 100 atmospheres simplified the complicated system of hydrated electron reactions found in irradiated water so that we could measure the rate constant reactions of e_{aq}^- with itself and with OH and H.

(b) In irradiated neutral solutions of tetranitromethane (TNM) reaction (1) takes place, (1) $e_{aq}^- + C(NO_2)_4 \rightarrow C(NO_2)_3^- + NO_2$. The nitroform ion formed in this reaction has a known extinction coefficient at 3660 A, so that by pulse irradiating aqueous TNM we have determined directly the extinction coefficient of e_{aq}^- at 5780. The extinction coefficient is essential for evaluating absolute rate constants in second order reactions, and can be used to determine $G_{e_{aq}^-}$ directly and thus perhaps settle the controversy concerning the proportions of H and e_{aq}^- formed in neutral solutions. A number of rate constants including that for $k_1 = 5 \times 10^{10}$ $\underline{M}^{-1}sec^{-1}$ were measured also. In the presence of oxygen it was possible to determine the equilibrium constant for the dissociation of the radical HO_2 to $H^+ + O_2^-$.

(c) Aqueous ferrocyanide is presently being studied to clarify discrepanices in earlier steady state radiolyses and to measure the equilibrium constant for the reaction $OH + OH^- \rightleftarrows O^- + H_2O$.

Future work includes pulse radiolysis studies in liquid ammonia and search for the OH radical absorption in water.

Publications:

S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani and J. K. Thomas, "Reaction Constants of the Hydrated Electron," J. Am. Chem. Soc., 85, 1375 (1963).

M. S. Matheson, "Formation and Detection of Intermediates in Water Radiolysis" Radiation Research Supplement, 4, 1 (1964).

[*] Hebrew University, Jerusalem, Israel

ARGONNE NATIONAL LABORATORY Chemistry Division

L. M. Dorfman/G. Czapski* 3/26/64

TRANSIENT SPECIES AND RATE CONSTANTS IN THE RADIATION CHEMISTRY OF OXYGENATED WATER

The pulse radiolysis technique has been used to study the optical absorption spectra and to determine the absolute rate constants for transient species in irradiated oxygenated aqueous solutions.

The absorption spectra of the hydroperoxy radical in its acid (HO_2) and basic (O_2^-) forms have been recorded. The HO_2 radical has a maximum at 230 mμ with a molar extinction coefficient of $\epsilon_{HO_2}^{230} = 1060\ M^{-1}Cm^{-1}$. The O_2^- has a maximum at 240 mμ with $\epsilon_{O_2^-}^{240} = 1150$. The pK for the conversion $HO_2 \rightleftharpoons O_2^-$ is 4.5. Absolute rate constants for the bimolecular disappearance are $k_{HO_2+HO_2} = 2.7 \times 10^6 M^{-1}sec^{-1}$ and $k_{O_2^-+O_2^-} = 1.7 \times 10^7 M^{-1}sec^{-1}$.

In strongly alkaline solution, two new long-lived absorptions were observed. One, with a maximum at 430 mμ is suggested to be O_3^-. The other, unidentified, has a maximum at 240 mμ.

Transient species in oxygenated water may play an important role in radiation biology so that a more complete understanding is desirable.

Publication:

L. M. Dorfman, I. A. Taub and R. Buhler, "Pulse Radiolysis Studies I. Transient Spectra and Reaction Rate Constants in Irradiated Aqueous Solutions of Benzene," J. Chem. Physics, 36, 3051 (1962).

G. Czapski and L. M. Dorfman, "Pulse Radiolysis V. Transient Spectra and Rate Constants in Oxygenated Aqueous Solutions," J. Phys. Chem., In press (May 1964).

---

*Hebrew University of Jerusalem, Jerusalem, Israel

2A46

ARGONNE NATIONAL LABORATORY Chemistry Division

M. S. Matheson/W. L. Buck*/K. Schmidt† 3/26/64

TRANSIENT CONDUCTIVITY IN PULSE IRRADIATED WATER

A differential amplifier has been constructed. This with other improvements has largely eliminated the tremendous electrical interference produced by the passage of the pulse of electrons through the conductivity cell. Preliminary measurements of the decay of the transient conductivity agree closely with the rate of decay predicted from rate constants measured in pulse radiolysis with optical detection, <u>if</u> plausible values of G of e^-_{aq}, of G of H^+ and of the mobility of e^-_{aq} are assumed. We have selected systems for study which should enable direct determination of these three quantities. From the mobility the diffusion constant of e^-_{aq} can be calculated, which is essential to understanding e^-_{aq} rate constants.

*Solid State Science Division
†Frankfort, Germany

2A47

ARGONNE NATIONAL LABORATORY Chemistry Division

M. S. Matheson/J. L. Weeks 3/26/64

PHOTOCHEMICAL STUDIES

The quantum yields of XeF_2 formation have been determined as a function of pressure, Xe/F_2 ratio, light intensity, etc. XeF_2 is probably formed by a step-wise addition of F atoms. The transient band spectra observed in flash photolysis probably are due to XeF. Dr. P. K. Carroll of the University of Chicago has analyzed the bands into several series from which the lower and upper state vibration frequencies can be determined. Work is continuing varying experimental conditions to try to obtain better spectra in flash photolysis (absorption) and also in emission using XeF_2 in a microwave discharge. Pulse radiolysis of gas phase mixtures of Xe and F_2 will also be tried as a way of obtaining transient spectra.

<u>Publications</u>:

J. L. Weeks and M. S. Matheson, "Photochemistry of the Formation of Xenon Difluoride," Noble Gas Compounds, H. H. Hyman, Editor, University of Chicago Press, p. 89 (1963).

J. L. Weeks and M. S. Matheson, "Xenon Difluoride," Inorganic Syntheses, Vol. VIII, in press (1964).

2A48

ARGONNE NATIONAL LABORATORY Chemistry Division

L. Kaplan/K. Wilzbach 3/26/64

RADIATION CHEMISTRY OF AROMATIC COMPOUNDS

The purpose of this program is to investigate the mechanisms of the changes produced in aromatic compounds by the action of various types of radiation. The approach used is that of detailed product identification and analysis, coupled with isotopic labelling to establish the route of formation of some of the more important products.

The radiolysis of the isomeric xylenes by gamma rays in the vapor phase produces, in addition to "polymer", smaller amounts of other products, many of which arise by loss, gain, or transfer of methyl groups. Ultraviolet photolysis appears to be a much more selective process, producing relatively large yields of isomer formed by migration of a methyl group to an adjacent position in the same molecule. Work is in progress using isotopic techniques, as well as the effect of added gases, of wavelength, and of other variables in an effort to establish the nature and structure of the excited molecule leading to isomerization. This work will be extended to related systems, such as the methylpyridines and to other forms of radiation. The detailed comparison will be made of the structures of the dimeric products produced from alkyl benzenes by ultraviolet photolysis with those formed by gamma radiolysis. Additional comparison will be made of radiolyses and photolyses in the liquid phase with those in the vapor phase.

2A49

ARGONNE NATIONAL LABORATORY Chemistry Division

W. A. Noyes, Jr. 3/26/64

ENERGY PATHS IN PHOTOCHEMISTRY

To determine in detail the fate of a quantum, i.e. to determine the fraction of absorbed light going into chemical reaction, fluorescence, phosphorescence and degradation to heat, it is necessary to measure the yield of each process accurately. Very few accurate yields for the quantum yield of fluorescence are available. Several methods are being tried in an effort to determine an accurate fluorescence yield for benzene. Benzene is the model compound chosen for a detailed study of all energy paths.

ARGONNE NATIONAL LABORATORY Chemistry Division

J. J. Katz/H. L. Crespi 3/26/64

PREPARATION OF ISOTOPICALLY ALTERED COMPOUNDS BY BIOSYNTHESIS

A considerable number of algae, bacteria, yeasts, and molds have been grown in a fully deuteriated form, and a wide variety of fully deuteriated compounds are now available from these organisms. The factors involved in the adaptation are still obscure, and clarification is highly desirable in the interests of extending the range of available deuteriated organisms. It is proposed to devote particular attention to the deuteriation of protozoa and higher plants, to add to the number of algae and molds that can be grown in D_2O, and to devise procedures for the isolation of fully deuteriated compounds. The nutritional quality of fully deuteriated algae and yeasts and their utility as deuteriating agents for higher animals will also be studied.

Publications:

H. F. DaBoll, H. L. Crespi and J. J. Katz, "Mass Cultivation of Algae in Pure Heavy Water," Biotech. Bioeng. 4, 281 (1962).

H. L. Crespi, M. Marmur, and J. J. Katz, "Use of Fully Deuteriated Algae Extracts for the Isolation of Nucleic Acids," J. Am. Chem. Soc. 84, 3489 (1962).

M. I. Blake, F. A. Crane, R. A. Uphaus and J. J. Katz, "Effect of D_2O on the Growth of Peppermint (Mentha piperita L.) I. Morphological Study," J. Pharm. Sci. 53, 79 (1964).

2A51

ARGONNE NATIONAL LABORATORY Chemistry Division

J. J. Katz/ H. L. Crespi 3/26/64

DEUTERIUM ISOTOPE EFFECTS IN PHOTOSYNTHESIS

Many fully deuteriated compounds and organisms are now available for the first time from various organisms cultivated in 99.8% D_2O. It is now possible therefore to study a variety of isotope effects hitherto inaccessible to investigation.

Chlorophyll and Other Chloroplast Pigments. Proton magnetic resonance applied to deuteriated compounds is a powerful tool for studying chemical reactivity since any hydrogen introduced in the molecule can readily be detected. It is proposed to investigate allomerization, hydrogen exchange, biosynthesis, and interactions of chlorophyll with other chloroplast pigments using deuterio-chlorophyll as the essential tool. These studies will be extended to chlorophylls of unknown composition present in photosynthetic bacteria and diatoms.

Isotope Effects on Photosynthesis and Hill Reaction. Photosynthesis and related phenomena in fully deuteriated algae are being investigated. Isotopically altered organisms should have unique utility for such studies, particularly for electron paramagnetic resonance applications.

Publications:

J. J. Katz, G. L. Closs, F. C. Pennington, M. R. Thomas, and H. H. Strain, "Infrared Spectra, Molecular Weights, and Molecular Association of Chlorophylls *a* and *b*, Methyl Chlorophyllides, and Pheophytins in Various Solvents," J. Am. Chem. Soc. 85, 3801 (1963).

J. J. Katz, R. C. Dougherty, F. C. Pennington, H. H. Strain, and G. L. Closs, "Hydrogen Exchange at Methine and C-10 Positions in Chlorophyll," J. Am. Chem. Soc. 85, 4049 (1963).

H. H. Strain, M. R. Thomas, and J. J. Katz, "Spectral Absorption Properties of Ordinary and Fully Deuteriated Chlorophylls *a* and *b*," Biochim. Biophys. Acta, 75, 306 (1963).

ARGONNE NATIONAL LABORATORY Chemistry Division

J. J. Katz/H. L. Crespi 3/26/64

DEUTERIUM ISOTOPE EFFECTS ON MACROMOLECULES

Many fully deuteriated compounds and organisms are now available for the first time from various organisms cultivated in 99.8% D_2O. It is now possible therefore to study a variety of isotope effects hitherto inaccessible to investigation.

Effects of Deuterium on the Properties of Macromolecules. Fully deuteriated proteins are being isolated and characterized by amino acid composition, ultracentrifugation, electrophoresis, and other physico-chemical procedures. The role of hydrophobic bonding is being studied by comparing thermal denaturation and γ-ray and neutron irradiation effects in ordinary and fully deuteriated proteins. Studies on nucleic acids are being extended along similar lines. Particular attention is being directed to the isolation, characterization, and reaction kinetics of fully deuteriated enzymes and substrates. The purpose of these studies is to ascertain the effects of isotopic substitution on macromolecular conformation and enzyme kinetics.

Publication:

D. S. Berns, H. L. Crespi, and J. J. Katz, "Isolation, Amino Acid Composition and Some Physico-Chemical Properties of the Protein Deuterio-Phycocyanin," J. Am. Chem. Soc. 85, 8 (1963).

2A53

ARGONNE NATIONAL LABORATORY Chemistry Division

M. H. Studier/E. N. Sloth/R. L. Niemann 3/26/64

HIGH TEMPERATURE CHEMISTRY

A. Surface Ionization

The effect of anionic constituents on the thermal ionization of alkali metal compounds from hot metal filaments of Pt, W, Ta and Re is under study. A modified Bendix time-of-flight mass spectrometer is employed to measure the relative intensity as well as the masses of the emitted species.

Variations in the isotopic ratio of Li^7/Li^6 with anionic constituents, evaporation rate and chemical reactions on hot surfaces is also being studied.

B. Laser Studies

A ruby laser is being used in conjunction with the Bendix time-of-flight mass spectrometer to study the molecular composition of materials at high temperatures.

ARGONNE NATIONAL LABORATORY Chemistry Division

R. J. Thorn/R. J. Ackermann/E. G. Rauh/
G. H. Winslow/R. R. Walters 3/26/64

HIGH TEMPERATURE CHEMICAL AND PHYSICAL INVESTIGATIONS I

The continuing investigations of chemical, physical, and thermodynamic properties of substances at high temperatures (1000-3000°K) are directed towards obtaining fundamental information about bonding in solids, liquids, and gaseous molecules. Exemplary projects in this category are the following:

1. One of the more significant contributions of thermochemical measurements at high temperature is the reliable determination of dissociation energies which demonstrate that the deformation of the valence electronic orbital contributes energies comparable to the binding energies in molecules having atoms with a number of low lying electronic states. Theoretical as well as experimental aspects of this behavior are being investigated.

2. Use of defect theories of nonstoichiometry and measured partial molar free energies (for example of oxygen in UO_{2+x}) enable one to derive the phase boundaries and interaction energies between nearest neighboring pairs in solids. X-ray (and possibly neutron) diffraction measurements are to be used to establish phase boundaries which in turn are to be used to derive thermochemical properties and averaged interaction energies between neighboring pairs of atoms.

Mainly compounds such as oxides, sulfides, carbides, phosphides, etc. of actinide elements are being investigated but in addition to the effusion method other techniques, such as molecular spectroscopy, electronic dissociation molecular beams, etc.

Publications:

R. J. Ackermann, E. G. Rauh and R. J. Thorn, "Thermodynamic Properties of Yttrium Monoxide; Correlation of Bonding in Group III Transition Metal Monoxides," J. Phys. Chem. 40, 883 (1963).

R. J. Ackermann and R. J. Thorn, "Chemical Bonding from High Temperature Studies," Adv. papers, Int. Symp. on High Temp. Tech., Stanford Research Institute, Sept. 1963.

ARGONNE NATIONAL LABORATORY Chemistry Division

R. J. Thorn/R. J. Ackermann/E. G. Rauh/
G. H. Winslow/R. R. Walters

3/26/64

HIGH TEMPERATURE CHEMICAL AND PHYSICAL INVESTIGATIONS II

Rate Processes

Integral parts of the investigations of the chemical and physical properties of substances at high temperatures are the complex rate processes occurring in them in both experimental and engineering systems. The following items represent the tenor of the studies:

1. Studies of the reversible nonequilibrium aspects of the thermodynamics of the vaporization process have helped to clarify the meaning of vaporization, condensation, and accommodation coefficients. The value of introducing such concepts as solid-like surface and gas-like surface phases has been illustrated. More definitive analyses are anticipated.

2. An investigation of the vaporization of uranium dicarbide has demonstrated that the rate is determined by the diffusion of uranium through a layer of carbon.

3. Studies of gas-solid interactions using molecular beams are anticipated.

The structural and thermochemical data and the theoretical concepts cited in Part A are being supplemented by the theories of reversible equilibrium and nonequilibrium rate processes.

Publications:

R. J. Thorn and G. H. Winslow, "Some Aspects of Thermodynamic and Transport Properties of the Uranium Dioxide Phase," submitted to panel at International Atomic Energy Agency, Vienna, Austria, March 1964.

K. D. Carlson, P. W. Gilles and R. J. Thorn, "An Analysis of Molecular Flow in an Isothermal Enclosure," J. Chem. Phys., 38, 2064 (1963).

R. J. Thorn and G. H. Winslow, "Vaporization Coefficient of Graphite and Composition of the Equilibrium Vapor," J. Chem. Phys., 26, 186 (1957).

ARGONNE NATIONAL LABORATORY Chemistry Division

H. Hoekstra/L. Fuchs 3/26/64

ULTRA HIGH PRESSURE, HIGH TEMPERATURE STUDIES

Work on the effects of ultra-high pressure on various chemical systems is continuing. Maximum temperatures and pressures used to date are 2000°C and 60 kbar. Although this does not represent the maximum capability of the tetrahedral apparatus, it does afford an extensive working range without subjecting the equipment to excessive strain or creating possible lengthy overhaul problems. Further extension of the working range is anticipated as it appears desirable.

Additional work has been completed on the uranium oxygen system. The stability range (temperature, pressure and composition) of the high pressure UO_3 phase is being outlined. Single crystals of β-U_3O_7 have been prepared at 1200°C and 40 kbar. These crystals will permit a detailed structural analysis of the compound (by S. Siegel) and lead to a better understanding of uranium-oxygen bonding in this portion of the phase diagram. High pressure studies on the UO_{2+x} phase indicate an inverse relationship between the extent of oxygen solubility in UO_2 and pressure.

The rare earth sesquioxides exist in three structural modifications, which have been designated (in order of increasing density): Type C (cubic), B (monoclinic), and A (hexagonal). At atmospheric pressure, the sesquioxides of the heaviest rare earths (Dy through Lu) exist only in the least dense, cubic form. At 300 kbar and 1000°C, dysprosium, erbium and ytterbium oxides have been converted to their corresponding monoclinic phases. Further work will be carried out at higher pressures to study conversion to the most dense, hexagonal configuration.

2A57

ARGONNE NATIONAL LABORATORY Chemistry Division

L. I. Katzin/A. Singh*/E. Gulyas/T. Burer† 3/26/64

OPTICAL ROTATORY DISPERSION SPECTROSCOPY

Optical rotation measurements, performed with high precision and detail, over a wide wavelength span and deeply into the ultraviolet, present what is in effect a spectroscopy which has hitherto been very poorly exploited. Computer analysis of such data, with least-squares fit to relations based on the Drude equation, gives unique insight into the relations of systems in which one or more components exhibit optical activity.

Study is underway on α-quartz, the optical activity of which is due to crystal geometry and not to an asymmetric center in a molecule. With the crystal structure of this material, and many of its other properties, well known, it is possible to attempt correlations of properties, and to study not only the material itself, but computational procedures.

Camphor, a classical study material, is being reviewed by the new techniques. Optical rotation is related to absorbing transitions in the molecular energy system. Camphor has a relatively isolated absorption peak which is optically active, and can be used for detailed observations of the relations between absorption and optical rotation. Solvent effects are also being studied. Other natural products will be investigated also.

Chemical reactions and chemical equilibria are also under investigation, with the techniques worked out for optical rotatory dispersion serving as indispensible tools. An example of such a system is the boric acid-tartaric acid complex system. Others are complexes of cations with active anions such as tartrate, complexes of boric acid and analogues with other optically active substances, and so forth.

Publications:

L. I. Katzin and E. Gulyas, "Thorium Tartrate Complexes by Polarimetry," J. Phys. Chem., 64, 1347 (1960).

L. I. Katzin and E. Gulyas, "Effects of Electrolytes on Rotatory Dispersion of Aqueous Tartrate Solutions," J. Phys. Chem. 66, 494 (1962).

---

*University of Alberta, Edmonton, Alberta, Canada

†Eidgen. Techn. Hochschule, Zurich, Switzerland

2A58

ARGONNE NATIONAL LABORATORY Chemistry Division

P. R. Fields/L. Stein/G. Toogood* 3/26/64

CHEMISTRY OF RADON

Radon has been found to react with fluorine to form a compound. Attempts to identify the formula or formulas of the radon fluoride(s) by time of flight mass spectrometry have not been completely successful. The fluorides are very active compounds and appear to react with parts of the spectrometer. Various techniques are being developed to complete the formula determinations. Attempts have been made to hydrolyze the fluorides and obtain radon compounds in solution similar to xenon chemistry. However, the radon fluorides are converted quantitatively to elemental radon under all hydrolysis conditions employed so far. Small amounts of radon may have been retained in solution, but this is not definite.

Several techniques have been used to try to produce other compounds of radon, e.g. oxides, chlorides, cyanides, without success.

Larger quantities of radium have been ordered to increase the quantity of radon used in this research. Many of the difficulties may be due to the trace amounts of radon used in the earlier experiments.

Publication:

P. R. Fields, L. Stein, and M. H. Zirin, "Radon Fluoride," J. Am. Chem. Soc., 84, 4164 (1962).

*Kings College, Durham University, Newcastle, England

2A59

ARGONNE NATIONAL LABORATORY Chemistry Division

M. H. Studier/E. H. Appelman/E. N. Sloth 3/26/64

CHEMISTRY OF ASTATINE

Seven day astatine-211, prepared by alpha bombardment on bismuth, has been reacted with iodine to produce AtI, which was identified mass spectrometrically. Reactions of astatine with other halogens are being studied.

In addition, the compounds HAt and CH_3At have been identified by mass spectrometry.

ARGONNE NATIONAL LABORATORY Chemistry Division

P. R. Fields/D. Cohen/W. T. Carnall/
G. Toogood[*]/A. Walker[†]

3/26/64

CHEMISTRY OF THE ACTINIDE ELEMENTS

Studies of the actinide elements in solution, in the solid and gaseous state are being carried out. Several new oxides of neptunium, Np_2O_5 and NpO_3 have been prepared and this phase of the work is being extended to plutonium and americium. Preparation of the actinide metals and compounds such as the oxides, halides, nitrides, and carbides are underway and a study of their structure is part of the program. The high temperature properties of some actinide oxides such as NpO_2 and PuO_2 are being investigated. Vapor pressure measurements on AmO_2 and CmO_2 will be made in the future.

Attempts to prepare AmF_6 have been unsuccessful although volatile compounds of the lighter actinides UF_6, NpF_6 and PuF_6 have been prepared. Additional attempts to prepare the volatile fluorides of Cm, Cf, and Es will be made when more material is available.

New separations techniques are investigated and developed, as well as improvements in existing techniques, especially in the areas of solvent extraction and ion exchange.

Studies on the oxidation of californium and einsteinium in aqueous solution using trace amounts of these elements have been underway. This investigation will be continued using sodium perxenate as the oxidizing agent.

Publications:

D. Cohen, "Oxides of Neptunium(V) and Neptunium(VI) from Molten Salts," Inorg. Chem. 2, 866 (1963).

S. Tsujimura, D. Cohen, C. L. Chernick, "The Attempted Preparation of AmF_6," J. Inorg. and Nucl. Chem. 25, 226 (1963).

S. Adar, R. K. Sjoblom, R. F. Barnes, and P. R. Fields, "Ion-Exchange Behavior of the Transuranium Elements in $LiNO_3$ Solutions," J. Inorg. and Nucl. Chem. 25, 447 (1963).

---

[*] Kings College, Durham University, Newcastle, England

[†] Nottingham University, Nottingham, England

ARGONNE NATIONAL LABORATORY Chemistry Division

P. R. Fields/W. T. Carnall/D. Cohen/
B. G. Wybourne/G. Toogood* 3/26/64

SPECTRAL STUDIES OF THE ACTINIDE AND LANTHANIDE ELEMENTS

The absorption spectra of the lanthanide and actinide elements in aqueous solutions, deuterated solvents,molten $LiNO_3$-KNO_3 and LiCl-KCl eutectics, and in certain crystals are being investigated. The energy of the transitions and the intensities or transition probabilities are being correlated with theory. The observed spectra are interpreted in terms of electronic strucutre and interaction of the lanthanide and actinide ions with surrounding ligand fields.

Divalent lanthanides and actinides, prepared by irradiating with high energy γ-rays the corresponding trivalent ions incorporated into a cubic crystal such as CaF_2 or $SrCl_2$ are also being examined by absorption spectroscopy. These ions show unusual spectra quite different than the forbidden trivalent ion transitions. Analogous to the lanthanides, the actinides may show possibilities as lasers in the divalent state.

New crystals of lanthanides and actinides in the form of double nitrates are being grown from molten salts. These salts are being used to provide a known crystal symmetry to compare absorption spectra with theoretical calculations for oscillator strengths.

Some work is in progress on fluorescence spectra of the actinide and lanthanide elements excited by light or gamma irradiation.

Publication:

W. T. Carnall, "The Near Infrared Transitions of the Trivalent Lanthanides, Th^{+3}, Dy^{+3}, Ho^{+3}, Er^{+3}, Tm^{+3}, Yb^{+3}," J. Phys. Chem. 67, 1206 (1963).

---

*Kings College, Durham University, Newcastle, England

ARGONNE NATIONAL LABORATORY Chemistry Division

P. R. Fields/W. T. Carnall/D. Cohen/A. Walker* 3/26/64

CHEMISTRY OF ACTINIDE ELEMENTS IN MOLTEN SALTS

Many aspects of the chemistry of actinide elements are conducted in molten salts. There are several reasons for requiring this type of media 1) the radiation decomposition is greatly reduced as compared to aqueous solutions 2) some molten salts are transparent to infrared light, and are thus good media for studying spectra in this region, 3) salts with desirable crystal symmetry crystallize from some molten salts and 4) some unusual oxidation states may be obtained in this non aqueous media.

The thermal decomposition of actinides to oxides in molten alkali nitrates if being studied. The oxides of Np, Pu, Am, and Cm are being prepared at fairly low temperatures for study.

Several higher oxides of neptunium have been prepared from molten salts. The preparation and examination of uranates, neptunates and plutonates from molten Li-K nitrate eutectic is continuing.

Molten $LiNO_3$-KNO_3 is used extensively as a solvent for the lanthanides and actinides to study the low lying excited states of these elements in the infrared region. This same salt eutectic is being used to grow the double nitrate salts of the lanthanides and potassium. Later actinides will be incorporated into this lattice. The double nitrate salts are being used to study the absorption spectra of the 4f and 5f electronic states and to interpret the interaction of these electrons with the surrounding ligand field.

Molten $LiClO_4$ is being used to prepare higher oxides and unusual modifications of normal oxides by dissolving various metals in this molten salt.

---

*Nottingham University, Nottingham, England

ARGONNE NATIONAL LABORATORY Chemistry Division

D. M. Gruen/R. L. McBeth/
H. Øye*

3/26/64

STUDIES IN FUSED SALTS

Studies of the absorption spectra of transition metal ions will be continued. One result of such studies on 3d metal ions has been the discovery of coordination number equilibria in fused salts. In a recent series of experiments it was shown that in molten aluminum chloride, the dipositive 3d ions are six coordinated, in contradistinction to the situation in alkali chloride melts where the same ions are four coordinated.

Detailed knowledge of the factors governing coordination number equilibria are being sought. To this end, our studies are being broadened in several directions to include:

1) Measurements on 4d, 5d and 5f ions
2) Effects due to varying the fused salt solvent composition
3) Influence of temperature
4) Influence of pressure

To measure the effects of pressure on the equilibria, an optical cell is being developed to operate at 30,000 p.s.i. inert gas pressure and temperatures in excess of 1000°C.

Publications:

D. M. Gruen, R. L. McBeth, Pure and Appl. Chem. 6, 23, (1963).

D. M. Gruen, Chap. 5 in Fused Salts, McGraw Hill Book Co., 1964 (in press).

H. Øye, D. M. Gruen, "Octahedral Absorption Spectra of Divalent 3d Metal Ions in Molten Aluminum Chloride," Inorg. Chem., June 1964 (in press).

---

*Technical University of Norway, Trondheim, Norway

2A64

ARGONNE NATIONAL LABORATORY Chemistry Division

L. Stein 3/26/64

PROTACTINIUM CHEMISTRY

Work will soon be resumed on protactinium chemistry. Five grams of Pa^{231} now on hand as Pa_2O_5 will be processed to remove niobium and other impurities, and protactinium fluorides and oxyfluorides will then be prepared for further characterization. The reduction of PaF_4 to protactinium metal will also be studied.

Publication:

Lawrence Stein, "Protactinium Fluorides," Proceedings of the Protactinium Chemistry Symposium, p, 57, Gatlinburg, Tennessee, April 25-26, 1963.

2A65

ARGONNE NATIONAL LABORATORY Chemistry Division

L. I. Katzin/E. Gulyas 3/26/64

PROPERTIES OF THE CHEMICAL BOND

(1) The rare earth ions have always been assumed to have little covalency, because of the electronic structure and the "burying" of the 4f levels made it plausible that no hybrid orbitals formed. Studies in this laboratory on certain systems, in non-aqueous solvent and in alkaline aqueous solution, have shown (in confirmation of certain phenomena noticed in the published data) that there are certainly rather strong covalency effects in the chemistry of the rare earths, and that correlated spectral alterations show considerable changes in the 4f electron energy levels. Work on covalency in the rare earths will be continued, to obtain information on coordination configuration effects, etc., such as have already been obtained for the d-elements.

(2) An indicator of metal ion-anion interaction, the case of polyatomic anions, is the change induced in the vibration pattern of symmetrical anions when they become bound to the cation. In solids in particular, clues to unexpected relations are found. Work on nitrates has been published; work on perchlorates has been temporarily interrupted but will be continued.

Publication:

L. I. Katzin, J. Inorg. Nucl. Chem. 24, 245 (1962), "Infra-Red Spectra of Nitrate Salts in Tributyl Phosphate Solution."

ARGONNE NATIONAL LABORATORY Chemistry Division

H. H. Hyman/J. G. Malm/C. L. Chernick/
H. Selig/L. Stein/ H. Claassen/I. Sheft 3/26/64

NOBLE GAS FLUORIDES

The initial discovery of xenon tetrafluoride led rapidly to the synthesis of other xenon fluorides and oxyfluorides, and krypton and radon compounds. Current research has concentrated on the hydrolysis products of xenon fluorides, and on problems arising from the somewhat unexpected properties of xenon hexafluoride.

Unlike all other known hexafluorides the spectra and behavior associated with xenon hexafluoride are not those expected of an octahedrally symmetrical molecule. This has led to extensive experimental research matched by intensive examination of the theories governing chemical bond formation and molecular symmetry.

The experimental aspects studied by the group include the development of a purification procedure via adsorption on sodium fluoride and measurement of the properties of the pure material, the preparation of acid-base complexes with fluoride ion acceptors ($XeF_6 \cdot BF_3$), and the investigation of the properties of the highly ionized solutions in hydrogen fluoride.

Raman spectroscopy of the yellow liquid XeF_6, and XeF_6 solutions, is difficult with conventional light sources. The early availability of Raman apparatus utilizing a red laser source will make an intensive study of such liquids more feasible.

Additional synthetic studies will center on krypton and radon compounds. Aqueous krypton chemistry may be a fertile field of research after the behavior of xenon compounds is more fully elucidated. Research on radon compounds will gradually shift from tracer scale studies to larger scale operations in the hot lab.

Publication:

H. H. Hyman, Ed., "Noble Gas Compounds," U. of Chicago Press (1963), pages 31, 35, 106, 113, 144, 167, 185.

2A67

ARGONNE NATIONAL LABORATORY Chemistry Division

H. H. Hyman/L. A. Quarterman 3/26/64

CHEMISTRY IN HYDROGEN FLUORIDE AND HALOGEN FLUORIDE SOLUTIONS

In this continuing program, electrical conductivity, infrared absorption, Raman spectra and nuclear magnetic resonance spectra have been observed and correlated with chemical properties.

Chain conductance for the proton in acid solution in hydrogen fluoride has been demonstrated, and a somewhat detailed picture is evolving of the behavior of fluoride ion acceptors in hydrogen fluoride.

Xenon fluorides in hydrogen fluoride and halogen fluoride solution offer a fertile field for investigation which we have barely touched.

In the near future this will take a large fraction of the available manpower, but we hope to continue at least some work on other fluorides.

The laser source will permit Raman studies of yellow colored solutions, not accessible with existing equipment. This will be especially valuable in ClF_3 and BrF_3 solutions.

Publications:

H. H. Hyman and L. A. Quarterman, "Hydrogen Fluoride Solutions Containing Xenon Difluoride, Xenon Tetrafluoride and Xenon Hexafluoride," Noble Gas Compounds, H. H. Hyman, Ed., U. of Chicago Press, p. 275 (1963).

H. H. Hyman, T. J. Lane and T. A. O'Donnell, 145th Meeting Am. Chem. Soc., p. 63T of Abstract, Sept. 1963.

ARGONNE NATIONAL LABORATORY Chemistry Division

M. H. Studier/D. L. Horrocks/E. N. Sloth 3/26/64

MASS SPECTROMETRIC STUDIES OF NOBLE GAS COMPOUNDS

The study of noble gas compounds by means of a modified Bendix time-of-flight mass spectrometer will be continued. Data on gaseous xenon fluoride and oxyfluoride, xenon tetroxide and krypton difluoride have been published. Ionic species containing two xenon atoms (from ion-molecule interactions) have been observed in the spectrometer.

The study of radon compounds and chemistry continues. Manipulation of these compounds is difficult because of surface effects. Compounds absorbed on the walls of the vacuum system are in general refractory and are decomposed on heating to give the spectrum of radon gas in the spectrometer. Attempts to prepare a volatile radon compound in systems made of different materials (metals, glass, organics) are underway.

A stable radon compound was formed in aqueous solution which carried on precipitated sodium perxenate.

Publications:

M. H. Studier, "Continuous Ion Source for a Time-of-Flight Mass Spectrometer," Rev. Sci. Instr. 34, 1367 (1963).

M. H. Studier and E. N. Sloth, "Noble-Gas Compounds," H. H. Hyman, Ed., Univ. of Chicago Press, Chicago, 1963, p. 47.

J. L. Huston, M. H. Studier and E. N. Sloth, "Xenon Tetroxide: Mass Spectrum," Science 143, 3611 (1964).

E. N. Sloth and M. H. Studier, "Gaseous Krypton Fluoride," Science 141, 528 (1963).

2A69

ARGONNE NATIONAL LABORATORY Chemistry Division

R. R. Chasman 3/26/64

THEORETICAL NUCLEAR CHEMISTRY

In the past year, an approach to the pairing Hamiltonian has been developed which bypasses most of the approximations and inaccuracies of the quasiparticle method. Our approach is sufficiently tractable to be computationally attractive, with the use of electronic computers (IBM-704 and CDC-3600). Calculations, done in the past year, indicate that our approach leads to excellent eigenvalues and eigenfunctions for the ground state and for broken pair states of the pairing Hamiltonian. The results of these studies have been discussed in the literature.

At present, we are attempting to describe, in some useful manner, those states of the pairing Hamiltonian which cannot be handled in terms of our previous work. This work will probably make use of large electronic computers.

Publications:

R. R. Chasman, "Eigenvalues of the Nuclear Pairing Hamiltonian," Phys. Rev. 132, 343 (1963).

R. R. Chasman, "Eigenfunctions of the Nuclear Pairing Hamiltonian," Phys. Rev. (in press) (1964).

ARGONNE NATIONAL LABORATORY Chemistry Division

P. Benioff/L. W. Person* 3/26/64

THEORETICAL STUDIES OF SIMPLE NUCLEAR REACTIONS AT HIGH ENERGY

We are interested in utilizing simple nuclear reactions (i.e., those involving only a few nucleons) induced by high energy protons to study nuclear properties of the target and product nuclei.

We have set up a program for the calculation of the distorted-wave impulse part of the exact T-matrix for the above cross-sections. Using various simple models for the nucleus, we shall then study the results to see how sensitive they are to the model assumptions. A comparison of the calculated and experimental cross-sections should tell us which model assumptions are good and should also give us some idea of the magnitude of the neglected terms in the exact T-matrix expression.

The calculation is being carried out with the CDC 3600 computer. It involves the evaluation of a sextuple integral which includes a three dimensional Fourier transform of an appropriately distorted single-particle wave function.

During the next year, we intend to apply the machine program to other types of nuclear reactions. We also will look into the higher order corrections to the distorted wave approximation as well as try to apply Feynman diagram techniques to the "simple" nuclear reactions.

---

*University of California, Berkeley, California

ARGONNE NATIONAL LABORATORY | Chemistry Division

S. Siegel/E. Sherry | 3/26/64

X-RAY DIFFRACTION STUDIES

The program on uranate structures is continuing. The following compositions are being investigated as part of a study of the uranyl bond: mono-uranates of Cr, Mn, Fe, Co, and Ti($TiUO_5$); di-uranates of Li, Na, K, and Rb; and tri-uranates of Mn, Co, Ni, Cu, and Zn. A form of uranyl borate, $UO_2(BO_2)_2$ has been obtained and is also being studied.

High pressure techniques have yielded single crystals of a new modification of UO_3, the zeta-form. The cell is orthorhombic with a = 7.511 Å, b = 5.466 Å, and c = 5.224 Å. The four uranium atoms are in general positions of $P2_12_12_1$ with x = 0.072, y = 0.131, and z = 0.033. Single crystals of β-U_3O_7 have also been obtained at high pressures. Preliminary studies indicate the small tetragonal cell as reported previously. However, powder x-ray and neutron diffraction data seem to indicate a larger cell or changed symmetry.

$K_3Pr_2(NO_3)_9$ is being investigated. The cell is cubic with a = 13.53 Å. Work on $CsCdCl_3$ has been completed. The cubic and hexagonal modifications exhibit the same structural relationships as is found for cubic and hexagonal $BaTiO_3$. X-ray studies of xenon compositions are primarily of a service nature as an aid in the development of the chemistry of these compounds.

The high temperature facility is in operation and temperatures near 1300°C have been obtained. It is hoped that temperatures of 2000°C can be reached with varying gas pressures over the sample.

Development of high and low temperature facilities for structural studies are now underway or contemplated.

<u>Publications</u>:

H. Hoekstra and S. Siegel, "Structural Studies on Li_4UO_5 and Na_4UO_5," J. Inorg. Nucl. Chem., In press (1964).

S. Siegel and E. Gebert, "The Structures of Hexagonal $CsCdCl_3$ and Tetragonal Cs_2CdCl_4," Acta Crystallographica, In press (1964).

ARGONNE NATIONAL LABORATORY Chemistry Division

F. S. Tomkins/M. Fred/A. Giacchetti/G. Smith[*] 3/26/64

EMISSION SPECTROSCOPY

The research program of the spectroscopy group has been expanded to include the spectra of all the elements from radium through californium. This includes the measurement of wavelengths, hyperfine structure, isotope shift, Zeeman effect, temperature classification, and absorption spectra, in order to derive energy levels and electron configurations. The expansion has been made possible through cooperative programs with the Lawrence Radiation Laboratory at Livermore and Berkeley; the Bellevue, France, Laboratory of the Centre National de la Recherche Scientifique; the Zeeman Laboratorium at Amsterdam, and Imperial College in London.

Some energy levels and electron configurations have now been obtained for all the elements through curium, with marked progress in the past year. The analysis and interpretation have been greatly aided by more effective use of computers and by theoretical calculations at Argonne and at Bellevue. Greatly improved exposures have been obtained for most of the above spectra, and future plans call for the continued measurement and interpretation of these data.

Our facilities have been enlarged to include a three meter vacuum spectrograph, currently being used for the investigation of the absorption spectrum of radium--in cooperation with Professor Garton of Imperial College. A further cooperative program is being initiated with the Physics Department of the University of Illinois to extend this technique to other elements, and to include kinetic spectroscopy.

Publications:

F. S. Tomkins and M. Fred, "Wavelength Measurements with a Concave Grating Spectrograph," Applied Optics 2, 715 (1963).

Th. A. M. von Kleef and M. Fred, "Zeeman Effect Measurements in Neutral and Singly Ionized Mercury," Physics 29, 389 (1963).

J. Blaise, M. Fred, S. Gerstenkorn and B. R. Judd, "Lowest Multiplet in the Arc Spectrum of Plutonium," Comptes rendues 255, 2403 (1962).

[*] Jesus College, Oxford University, Oxford, England

ARGONNE NATIONAL LABORATORY Chemistry Division

J. Weil/J. Heidberg*/M. Mori**/M. Okada†/P. M. Wright‡ 3/26/64

MAGNETIC RESONANCE STUDIES

Magnetic resonance provides a powerful tool for study of unpaired spin systems, and gives detailed information both about steady-state molecular structure and about dynamic phenomena involving motions of atoms and electrons. At present, paramagnetic resonance studies of radiation damage centers and charge-transfer phenomena in quartz, and of delocalized electron systems in peroxodicobalt complexes are being carried out. Study of the chemistry of hydrazyl-type free radicals continues to be very fruitful, and numerous new reactions and substances are being investigated. Substituted picryl-hydrazines and other aromatic nitro-compounds exhibit proton magnetic spectra giving considerable insight into dynamic aspects of mesomeric and steric effects in these molecules. Studies of the theory of various aspects of spin resonance have centered largely on the effects of molecular motions and randomness of their orientations on the parameters describing solution and powder spectra, as well as on the inter-relationship between crystal symmetry and magnetic resonance parameters in single crystal studies.

Publications:

P. M. Wright, J. A. Weil, T. Buch and J. H. Anderson, "Titanium Colour Centres in Rose Quartz," Nature 197, 246 (1963).

J. A. Weil, G. L. Goodman and H. G. Hecht, "Paramagnetic Resonance Absorption in Peroxo-Dicobalt Complexes - Single Crystal Studies," Paramagnetic Resonance V. II, p. 880, (W. Low, Editor) Academic Press (1963).

J. A. Weil and H. G. Hecht, "On the Powder Line Shape of EPR Spectra," J. Chem. Phys. 38, 281 (1963).

---

*Frankfort, Germany

**Osaka City University, Osaka, Japan

†Government Chemical Industrial Research Institute, Tokyo, Japan

‡Wheaton College, Wheaton, Illinois

2A74

ARGONNE NATIONAL LABORATORY Chemistry Division

M. Atoji 3/26/64

NEUTRON DIFFRACTION STUDIES

The neutron coherent-scattering amplitude of naturally occurring Hf has been established as + 0.785 Fermi unit at 0.08 to 0.03 ev and the multi-level Breit-Wigner calculation including the bound-level effect led the reaction nuclear radius of 0.94 Fermi unit in agreement with the optical model with a diffuse spherical potential. The method has been extended to other heavy elements with special reference to their imaginary-part scattering amplitudes. The M_3C (M = rare earth and Y) structure, cubic by x-rays, was found to be monoclinic in its atomic symmetry and further studies on the magnetic-spin arrangement in Tb_3C are under progress. The neutron investigations on $AlCr_2$, Cr_3C_2, CbC, TaC, TiC and other related metal carbides are nearly complete. The structure-analysis programs on Mg_2C_3, MgC_2, Li_2C_2, Na_2C_2, $LiHC_2$, KHC_2 and Pu_2C_3 have not been fruitful, because of poor quality samples. Further effort is being made on obtaining better purity compounds.

The instrumental activities on our automatic double-crystal neutron diffractometer are represented by: some additional improvements on the magnetic devices (max. 18 K oersted) for temperature range, 1.6°K to 1700°C; modification on the high-temperature furnace for non-magnetic study; electronics addition for improved automation.

Future program includes the following: the structure and magnetic analyses on various carbides, acetylides and peroxides; the interaction between conduction and magnetic electrons in magnetite; the electrostatic field effect on magnetic compounds; single-crystal preparation by means of bridgman, Czochralski, electron-beam floating zone-refining and stress-annealing techniques.

Publication:

M. Atoji, "Slow-Neutron Cross Sections of Hafnium," in press, Acta Crystallographica, (1964).

ARGONNE NATIONAL LABORATORY Chemistry Division

G. L. Goodman 3/26/64

THEORETICAL STUDIES IN MOLECULAR QUANTUM MECHANICS

A recent reinterpretation of the vibrational spectra for certain metal hexafluoride molecules has yielded information about the size of the interaction between electronic motions and nuclear motions in these molecules. This information is now being used to predict the properties to be expected for the higher energy electronic states of these and related hexafluoride molecules: (ReF_6, OsF_6, IrF_6, PtF_6, TcF_6, RuF_6, RhF_6). Eventually, these predictions will be compared with spectral features of these molecules in order to confirm that the unusual features in their spectra arise from dynamic Jahn-Teller effects.

The molecule XeF_6 was not included in the original work on molecular dynamics of hexafluoride molecules. There is strong evidence however, that the properties of this molecule are seriously influenced by interactions of electronic and nuclear motions. The study of this problem and the search for other examples of vibronic coupling is well under way.

One by-product of this work has been the extension of a perturbation formula given by Moffitt and Thorson to yield a perturbation theory based entirely on commutators of quantum mechanical operators. The possible uses of this new way of treating perturbations are being investigated. They include the calculation of vibronic energy levels and wave functions, the relatively easy development of spin-Hamiltonians to any order in the hyperfine interaction constants, and perhaps the calculation of atomic correlation energies and molecular bond energies.

Publications:

B. Weinstock and G. L. Goodman, Adv. in Chem. Phys., 6, 000 (in press)(1964).

G. L. Goodman, Abstracts of papers presented at the Chemical Society Anniversary Meetings, Birmingham, England, April 4-9, 1964, "Theories of Bonding for Xenon Fluorides."

2A76

ARGONNE NATIONAL LABORATORY — Chemistry Division

B. G. Wybourne — 3/26/64

THEORETICAL INVESTIGATIONS OF THE SPECTROSCOPIC PROPERTIES OF ATOMS AND IONS

This project represents an attempt to interpret the very complex spectra of the lanthanides, and more especially, the actinides. Three aspects of this project are currently under study:

1. The effects of configuration interaction on the energy levels of atoms and ions in the gaseous, liquid and solid state. Extensive use of Racah's algebra of tensor operators is being made to obtain a simple phenomenological treatment of these effects.

2. Atomic energy level calculations. The exceedingly complex spectra of the actinides can only be understood if the existent experimental studies are backed by a theoretical attack upon the calculation of atomic energy levels. Computer techniques are being used to calculate the necessary energy matrices and to analyze the spectra.

3. Transition probabilities and crystal spectra. A detailed study of the intensities of optical transitions in solutions and solids containing actinide ions is being undertaken to investigate the behavior of different ligand fields and to predict the intensity characteristics of the, as yet unobserved, spectra of several heavy actinides, attention is also being given to the interpretation of the crystal spectra of the actinides.

ARGONNE NATIONAL LABORATORY Chemistry Division

P. Day 3/26/64

ASYMMETRIC ROTOR NUCLEAR MODEL

During the past year further modifications have been made on the collective model originally advanced by Bohr and Mottelson over a decade ago to explain the observed level structure in deformed nuclei. Although the initial model was advanced on the basis that nuclei has cylindrical symmetry, these recent modifications indicate that the nucleus is not symmetrical in various regions of the periodic table. Several years ago Davydov attempted to set up the collective model for even nuclei without restricting the nuclei to cylindrical symmetry. In a series of papers over the last few years, he has successively been able to solve his equation sets with fewer and fewer approximations. In his latest attempt he has been able to take into account the effect of the "gamma vibrations" in an exact manner.

The numerical evaluation of the results is rather complex. Since the equations are not in explicit form and are a function of four parameters, it was necessary to evaluate the equations over a fairly large range with a sufficiently find mesh and then use an interpolation scheme in order to compare the model with experimental results. A computer program was used to produce an extensive table on the IBM-704. Since graphical interpolation would be a time-consuming task by hand, a program has been written to perform tri-variate inverse interpolation on the computer.

Although the previous modifications on the model improved the agreement with experiment, the present modification is in rather poor agreement with the latest experimental results on even nuclei. This may be due to an error in the numerical evaluation of the equations or else the approximations used by Davydov are inadequate in the rare earth mass region.

Further detailed comparison with experimental data and a detailed analysis of the Davydov approximations is planned in order to determine why a heretofore successful theory appears to be less applicable after undergoing a so-called "improvement."

ARGONNE NATIONAL LABORATORY Chemistry Division

H. R. Hoekstra 3/26/64

URANIUM-OXYGEN BONDING

Bonding between hexavalent uranium and oxygen is generally unsymmetrical - two short (uranyl) bonds are formed, together with four, five or six longer secondary bonds. The purpose of this investigation is to obtain an understanding of the various types of bonding encountered in the uranyl salts, uranium(VI) oxides and the metal uranates. At present, the study is concerned principally with the synthesis of pure compounds in the three categories listed above, the determination of their crystal structures (in cooperation with S. Siegel) and infrared spectra, and the correlation of these data to arrive at uranium-oxygen bond lengths and bond orders.

One of the compounds under investigation at the present time is uranyl metaborate ($UO_2B_2O_4$), which appears to have the greatest thermal stability of any known uranyl salt. Its decomposition temperature is ~1100°C. The structure of $UO_2B_2O_4$ is being studied; the infrared spectrum is indicative of a typical uranyl salt with a $U\text{-}O_I$ bond length of ~1.7 Å.

Several groups of metal uranates have been prepared. Results on the alkali metal uranates show a good correlation between uranate composition (in the various members of the series $M_2U_xO_{3x+1}$) and uranyl bond length, as predicted by the Zachariasen bond length-bond strength rule. Similar correlations are evident among the alkaline earth and transition metal uranates (Ti through Zn).

Publication:

H. R. Hoekstra and S. Siegel, "Structural Studies on Li_4UO_5 and Na_5UO_5," J. Inorg. Nucl. Chem., in press (1964).

2A79

ARGONNE NATIONAL LABORATORY Chemistry Division

B. M. Abraham/D. W. Osborne/Y. Eckstein*/
J. B. Ketterson*/R. A. Guenther†

3/26/64

PROPERTIES OF LIQUID HELIUM-3 AND LIQUID HELIUM-4 AT LOW TEMPERATURES

Studies of He^3 and He^4 at low temperatures are of importance theoretically and experimentally because of the occurrence of quantum effects on a macroscopic scale. Further, He^3 is the only uncharged Fermi-Dirac system available for investigation. Since the theoretical predictions about liquid He^3 are valid only in the limit of very low temperatures, attempts are being made to test the predictions experimentally below 0.1°K.

Heat capacity measurements are now being made on liquid He^3 from 0.04 to 0.5°K. Although this temperature range has been covered by two publications from other laboratories, the divergence between the two are too great to provide an adequate test of the theories. It is hoped that the current work will resolve the ambiguities.

An apparatus has been constructed to measure the attenuation of high frequency sound in liquid He^3 in an attempt to detect the presence of "zero sound." This is a new type of sound vibration predicted by Landau which can be exhibited only by Fermi-Dirac systems.

Measurements of the viscosity of liquid He^3 are also planned in the temperature range 0.01 to 0.4°K, and the results will be compared with the theoretical $1/T^2$ dependence.

---

*Solid State Science Division

†Illinois Institute of Technology, Chicago, Illinois

ARGONNE NATIONAL LABORATORY Chemistry Division

D. W. Osborne/B. M. Abraham/H. E. Flotow/
F. Schreiner

3/26/64

LOW TEMPERATURE CALORIMETRY

The primary purpose in making low temperature heat capacity measurements is to obtain thermodynamic functions such as entropy, enthalpy, and free energy increments which are needed in thermodynamic calculations. Another purpose is to obtain information regarding lattice dynamics, antiferromagnetic and ferromagnetic transitions, order-disorder transitions, ligand field splitting of the ground electronic state, and other interesting solid state phenomena.

Measurements have been completed down to 5°K on a number of metal hydrides and deuterides, and the heat capacity curves have been analyzed to determine the characteristic hydrogen vibration frequencies. Similar work is planned on rare-earth hydrides. Also it is planned to make further measurements on the heat capacities of these and other hydrides from 0.8 to 15°K and to attempt to resolve the heat capacity curves into lattice, electronic, and magnetic contributions. Further work is planned on alpha- and beta-UH_3.

Calorimetric measurements have been made on several hexalfuorides: NpF_6, MoF_6, and TcF_6. Because these compounds are volatile at room temperature it has been possible to compare the entropies computed from the third law of thermodynamics with the entropies computed from the electron diffraction and spectroscopic data and thus to obtain a check on the interpretation of the spectra. Similar studies will be made of the new compounds XeF_2, XeF_4 and XeF_6.

Heat capacity measurements will also be continued on compounds of rare earths, thorium, uranium, and neptunium.

Publications:

H. E. Flotow, D. W. Osborne, K. Otto, and B. M. Abraham, "YH_3 and YD_3: Heat Capacities and Thermodynamic Functions from 15° to 350°K and Infrared Absorption Spectra," J. Chem.Phys. 38, 2620 (1963).

H. E. Flotow, D. W.Osborne, and K. Otto, "Heat Capacities and Thermodynamic Functions of YH_2 and YD_2 from 5° to 350°K and the Hydrogen Vibration Frequencies," J. Chem. Phys., 36, 866 (1962).

ARGONNE NATIONAL LABORATORY
Chemistry Division

L. B. Magnusson
3/26/64

ION-ION AND ION-SOLVENT INTERACTIONS

Correlative studies of the formation of 1:1 complexes in aqueous solution of noble gas type cations with fluoride ion and with the anions of o-carbonyl phenols suggest some new approaches to the theories of ion-ion and ion-water interactions. Previous theories treat the interactions as being independent of the sign of the ion charge. The present correlations indicate that the cationic and anionic interactions are fundamentally different. The cation charge may be screened and effectively delocalized by a covalent bonding of solvent electrons. Anion charge cannot be screened and the anomalies in the ionic theories may be the result of a greater extension of a vacuum electric field into the surrounding solvent. Accurate data will be secured for the first hydrolysis constants of noble gas type cations. Correlation of the data may give further information on the anion field. Thought is being given to the feasibility of direct measurement of individual cation and anion hydration energies. The information, very difficult to obtain, would provide answers to the most important problems in electrolyte theory.

Publications:

L. B. Magnusson, "Short Range Interactions of Aqueous Ions," J. Chem. Phys. 39, 1953 (1963).

L. B. Magnusson, C. Postmus, Jr., and C. A. Craig, "Coordination in Solutions. V. Formation Constants for 1:1 Complexes of o-Carbonyl Phenols with Ca, Sr, Ba, La, Eu, Lu, Sc, Y and Th Ions in Water," to be submitted to J. Am. Chem. Soc.

ARGONNE NATIONAL LABORATORY Chemistry Division

L. B. Magnusson/C. Postmus, Jr./C. A. Craig 3/26/64

INTER- AND INTRAMOLECULAR HYDROGEN BONDING IN AQUEOUS SOLUTION, METAL ION CHELATE COMPLEXES, AND THE pH SCALE

The discovery that a glass electrode cell with a reproducible saturated KCl junction can give the activity of hydrogen ion may be very important to electrolyte theory. Preliminary indications are that cations and anions have detectably different activity coefficients. Further work is planned using more sensitive equipment. The strengths of hydrogen bonds are important in bidentate ligands which can chelate metal ions or hydrogen ions. In phenol derivatives with a carbonyl group and a nitro group each ortho to the hydroxyl group, the possibility exists in aqueous solution of competitive intra- as well as intermolecular bonding. Recent work suggests there is little bonding to an ortho nitro group although an intramolecular bond exists in organic solvents. The work will be extended to D_2O systems. A systematic correlation of pK values with nuclear magnetic resonance has led to an unambiguous assignment of all the monochloro-derivatives of salicylaldehyde.

Publication:

L. B. Magnusson, C. Postmus, Jr., and C. A. Craig, "Coordination in Solutions. I. Acid Strengths of Phenol Derivations in Water," J. Am. Chem. Soc., 85, 1711 (1963).

ARGONNE NATIONAL LABORATORY — Chemistry Division

D. M. Gruen/F. A. Cafasso/C. Thalmayer — 3/26/64

MAGNETIC SUSCEPTIBILITY STUDIES

Magnetic susceptibility measurements are being carried out on selected compounds in the range 2-300°K and at a series of magnetic field values. The Faraday method is employed on ~100 mg of sample.

Recent results have included data on ReF_6 and UCd_{11}.

Measurements are in progress on actinide sulfides and on XeF_6. In the latter compound, theory predicts a low lying triplet state. It is hoped that the magnetic measurements can throw light on this interesting hypothesis.

Publications:

H. Selig, F. A. Cafasso, D. M. Gruen and J. G. Malm, "Magnetic Susceptibility of ReF_6," J. Chem. Phys. 36, 3440 (1962).

F. A. Cafasso, H. M. Feder and D. M. Gruen, "Electronic Configuration and Valency of Uranium in UCd_{11}, a Magnetically Dilute Alloy," J. Chem. Phys. 38, 1256 (1963).

ARGONNE NATIONAL LABORATORY Chemistry Division

J. C. Hindman 3/26/64

APPLICATION OF NUCLEAR MAGNETIC RESONANCE TO THE STUDY OF STRUCTURE IN ELECTROLYTE SOLUTIONS

The successful development of a model for the interpretation of the effects of 1-1 electrolytes on the proton resonance of water suggested that one could expect to obtain significant information about the structure of liquid water itself from a similar treatment. It has been found that the shielding changes associated with the transformation of water vapor to ice can be used to calculate the dipole moment of the water molecule in ice. Extension of the model to a detailed description of the liquid structure as a function of temperature is in progress. The principal remaining factor to be considered is the second-order van der Waals-London effect on the chemical shift.

The interpretation of the experimental observations on the effect of temperature on the proton resonance in solutions of 1-1 electrolytes is in progress.

Further work is to be oriented toward the interpretation of dynamic processes in electrolyte solutions. It is expected that the greater degree of complexity in the dynamic behavior will require extension of the experimental measurements to nuclei other than hydrogen in order to provide an adequate basis for extension of the theoretical treatment. It is further expected that by a suitable combination of static and dynamic measurements further information can be obtained about rates of exchange of water between solvent and hydrated ions, order in outer hydration layers, rates of complex ion formation, outer sphere association and related phenomena.

Publication:

J. C. Hindman, "Nuclear Magnetic Resonance Effects in Aqueous Solutions of 1-1 Electrolytes," J. Chem. Phys. 36, 1000 (1962).

2A85

ARGONNE NATIONAL LABORATORY
Chemistry Division

D. A. Hutchison
3/26/64

RESEARCH APPLICATIONS OF MASS SPECTROMETRY

Experimental Threshold Laws for Ionization in the Rare Gases

Experimental threshold laws for ionization by electron impact in the rare gases have been determined. It has been found within the limits of experimental precision that ionization varies directly with the first power of the electron energy in excess of the ionization potential. The data do not agree with a 1.127 power law predicted by one theory.

The energy-selected electron beams employed in these experiments were obtained by use of a parallel-plate electrostatic energy selector. A second parallel-plate analyzer furnished information on the electron-energy distributions used in producing ionization. Distributions have been measured for beams selected at 25.0 to 7.5 volts energies. Beams selected at 3.5 volts have been used in studies of ionization in the rare gases. Electronic differentiation of ion-appearance-potential curves was obtained by superposing a sinewave voltage signal on the electron beam and measuring the amplitude signal generated in the ion beam. Computer calculations of the integral of the product of the electron-energy-distribution functions and assumed first order threshold functions yield ionization intensity functions and their first derivatives with energy in close agreement with experimentally measured ones.

Noise in the ionization signals appears to be our most important adverse problem at present. We plan to alleviate this by addition of a digital storage oscilloscope to our instrumentation. Random noise should average toward zero while the stored signal should be enhanced thus increasing the signal-to-noise ratio.

2A86

ARGONNE NATIONAL LABORATORY Chemistry Division

D. F. Peppard/G. W. Mason 3/26/64

THE PHYSICAL CHEMISTRY OF THE INTERACTION OF (X)(Y)PO(OH) EXTRACTANTS WITH HYDROGEN BOND DONORS AND ACCEPTORS

The molecular complexity of (X)(Y)PO(OH) compounds in a variety of diluents ranging from alkanes, such as n-heptane, through benzene, carbon tetrachloride, di-alkyl ethers such as di n-butyl ether, and ketones such as methyl iso butyl ketone to alcohols such as n-decyl alcohol and liquid carboxylic acids such as 2-ethyl hexanoic acid is being studied. The groups X and/or Y may be aryl (Ar-), aroxy (ArO-), alkyl (Alk-), alkoxy (AlkO-), hydrogen (H-), or hydroxy (HO-), or a substituted variant.

In general, if neither X nor Y is hydroxy, these compounds tend toward the dimeric state in benzene and the monomeric state in alcohols. For $(X)PO(OH)_2$ where X is not hydroxy the molecular complexity is hexameric or greater in benzene, usually higher than this in n-heptane, and much lower in good hydrogen bond acceptors. For example (2-ethyl hexyl $O)PO(OH)_2$, is monomeric in methyl alcohol and approximately dimeric in acetone. However, (2-ethyl hexyl$)PO(OH)_2$, which differs only in that a C-O-P bond has been replaced by a C-P bond, has a molecular complexity nearly three times as great.

A study of the state of aggregation of $(X)PO(OH)_2$, where X includes a variety of alkyl and aryl groups as well as $Ar-O-CH_2CH_2O-$ and $Alkyl-O-CH_2CH_2O-$ groups is nearing completion and will be reported in the literature in conjunction with relevant extraction data including actinide and lanthanide cations.

Publications:

D. F. Peppard and G. W. Mason, "Some Mechanisms of Extraction of M(II), (III), (IV), and (VI) Metals by Acidic Organophosphorus Extractants," Nuclear Science and Engineering 16, 382 (1963).

J. R. Ferraro and D. F. Peppard, "Structural Aspects of Organophosphorus Extractants and Their Metallic Complexes as Deduced from Spectral and Molecular Weight Studies," Nuclear Science and Engineering 16, 389 (1963).

ARGONNE NATIONAL LABORATORY Chemistry Division

John R. Ferraro 3/26/64

PHYSICAL CHEMISTRY OF ACIDIC ORGANOPHOSPHORUS COMPOUNDS AND VARIOUS INORGANIC SALTS

Proton magnetic resonance studies on acidic organophosphorus compounds are being expanded to include the following studies: (1) Mixtures of organophosphorus compounds (2) Organophosphorus compounds with other materials (3) Dibasic organophosphorus acids of the type $(GO)PO(OH)_2$, $GPO(OH)_2$. Recent work on the acids $(GO)_2PO(OH)$, $(GO)G'PO(OH)$ and $G_2PO(OH)$, and a PMR study of new chelates involving organophosphorus compounds are presented in attached reprints.

Also in progress are Raman and far infrared studies (350-70 cm^{-1}) of solid inorganic compounds (e.g. transition-metal nitrates, carbonates, bromates, iodates, etc.). Attempts will be made to differentiate between external vibrations (due to the lattice) and internal vibrations (e.g. M-O fundamentals)in the far infrared region. This information will lead to conclusions on the degree of covalency present in these salts. Similar studies are being made with the hydrogen bonded organophosphorus acids in search of low-lying hydrogen bonded fundamental vibrations. The presence or absence of these frequencies will help in elucidating the nature of the hydrogen bonding in these acids, since x-ray studies are lacking.

Publications:

J. R. Ferraro and D. F. Peppard, "Proton Magnetic Resonance Studies of Acidic Organosphosphorus Compounds," J. Phys. Chem. 67, 2639 (1963).

J. R. Ferraro, "Proton Magnetic Resonance of Several New Chelates," J. Inorg. Nucl. Chem., 26, 225 (1964).

2A88

ARGONNE NATIONAL LABORATORY Chemistry Division

D. F. Peppard/G. W. Mason 3/26/64

THE ACID STRENGTH OF (X)(Y)PO(OH) AND ITS EXTRACTANT EFFECTIVENESS AS A FUNCTION OF X AND Y

Each member of the series of compounds, (X)(Y)PO(OH), where X and/or Y may be phenyl(C_6H_5-), cyclo-hexyl(C_6H_{11}-), hydrogen (H-), phenoxy (C_6H_5O-), cyclo hexoxy ($C_6H_{11}O$-) or hydroxyl (HO-), with two exceptions, has been prepared and purified. The exceptions are (C_6H_5O)(H)PO(OH) and ($C_6H_{11}O$)PO$(OH)_2$- the former proving unstable and the latter not isolatable with the techniques currently available. Each compound has been titrated in both 75% ethanol and 95% ethanol with 0.1 molar NaOH in the same medium under a standard set of conditions.

The pK_A values have been computed from the titration data. Numerical values were then assigned individually to the phenyl, cyclo hexyl, hydrogen, phenoxy, cyclo hexoxy, and hydroxy groups so that by combining the values for the X and Y present the pK_A of the compound is closely approximated. A report of this phase of the investigation is now being prepared for publication.

The pK_A data will be correlated with the Hammett Acidity Function values now being obtained.

They will also be correlated with the numerical values of the extractant coefficients, K, determined under a standard set of conditions for selected metallic cations.

Publication:

J. R. Ferraro and D. F. Peppard "Proton Magnetic Resonance Studies of Acidic Organo-phosphorous Compounds," J. Phys. Chem. 67, 2639 (1963).

2A89

ARGONNE NATIONAL LABORATORY Chemistry Division

D. F. Peppard/G. W. Mason 3/26/64

APPLICABILITY OF (X)(Y)PO(OH) EXTRACTANTS TO ACTINIDE AND LANTHANIDE SEPARATIONS AS A FUNCTION OF X AND Y

A series of (X)(Y)PO(OH) compounds in which X and/or Y may be aryl (Ar-), aroxy (ArO-), alkyl (Alk-), alkoxy (AlkO-), hydrogen (H-) of hydroxy (HO-), or substituted variants of the above, has been prepared and studied as extractants for actinides and lanthanides.

Although M(II), M(III), M(IV), M(V) and M(VI) are all being investigated, the major emphasis is on M(III). Separations involving any other than M(III) are very readily accomplished, but the M(III) mutual separations remain difficult.

No separations involving actinides (III) or lanthanides (III) by use of $(Ar)_2PO(OH)$, $(Alk)_2PO(OH)$, (Ar)(Alk)PO(OH), (Ar)(H)PO(OH), (Alk)(H)PO(OH), $(Alk)PO(OH)_2$, or $(Ar)PO(OH)_2$ have been reported previously.

Examples of these unreported types of extractants as well as the other formulations will be studied with the hope of obtaining better mutual separations of M(III) species, especially in the region beyond curium. The stoichiometry of the extraction is also being investigated on at least one example of each of the type extractants.

The effect of carrier diluents will also be studied, both from the points of view of polarity and of generalized interaction between extractant and carrier diluent, and the point of view of change in state of aggregation of extractant. (The term carrier diluent is used in preference to inert diluent, since inertness seems hardly consistent with the observed large effects of diluent change.)

In the state of aggregation studies di 2-ethyl hexyl phosphoric acid, $(C_2H_5 \cdot C_6H_{12}O)_2$ PO(OH), (HDEHP) and di para (1,1,3,3-tetramethyl butyl phenyl) phosphoric acid, $(C_8H_{17} \cdot C_6H_4O)_2PO(OH)$, (HDOΦP) have been used as extractants in *n*-decyl alcohol, $C_{10}H_{21}OH$, in which they are monomeric, in contrast to their dimeric states in benzene, etc. A report of this phase of the work has been submitted for publication.

Publication:

D. F. Peppard, G. W. Mason and C. M. Andrejasich, "Applicability of Certain Organo Phosphorus Extractants to Environmental and Biological Radioactivity Surveys," J. Inorg. Nucl. Chem. **25**, 1175 (1963).

2A90

ARGONNE NATIONAL LABORATORY Chemistry Division

E. P. Horwitz/L. J. Basile 3/26/64

TRANSPLUTONIUM ELEMENT SEPARATIONS CHEMISTRY

The over-all purpose of our investigation is to obtain information on the transplutonium elements that will be of use in the separation of these elements. Concurrently some aspects of the chemistry of the transplutonium elements will also be investigated.

The application of zirconium phosphate gels for use as an ion exchange medium for the separation of transplutonium elements is currently being investigated. By controlling and changing certain variables it is hoped that conditions will be obtained whereby certain transplutonium elements can be separated as a group and also from each other.

The use of polyaminopolycarboxylic acids as chelating agents for the transplutonium elements is also being investigated. A study of the physical and chemical properties of these chelates both as solids and in solution might lead to improved methods in separation and possible practical applications for transplutonium elements.

SECTION 2B

ARGONNE NATIONAL LABORATORY - CHEMICAL ENGINEERING DIVISION

2B1 Solubility of Rare Gases in Alkali Metals

2B2 Thermodynamics - Binary Alkali Metal Solutions

2B3 Thermodynamics of Liquid Metal Solutions

2B4 Phase Studies by the Effusion Method

2B5 Magnetic Susceptibility Studies

2B6 Lithium Hydride Regenerative Cell

2B7 Bimetallic Regenerative Cells

2B8 Solubility of Intermetallic Compounds in Fused Salts

2B9 Regenerative Cell Kinetics

2B10 The Enthalpies of Formation of the Diborides of Some Group IV and V Metals

2B11 The Enthalpies of Formation of Silicon Carbide and Tetrafluoromethane

2B12 The Enthalpies of Formation of Uranium Compounds

2B13 The Design and Construction of a 1500°C High Precision Enthalpy Increment Drop Calorimeter

For further information on completed work, the reader is referred to the open scientific literature and to the Argonne National Laboratory Chemical Engineering Division Research Highlights Report for May 1963 through April 1964, ANL-6875.

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

H. M. Feder/I. Johnson/S. K. Dhar March 13, 1964

SOLUBILITY OF RARE GASES IN ALKALI METALS

Data on the solubility and temperature coefficient of the solubility of rare gases in liquid alkali metals may be used to compute thermodynamic quantities for the dissolved rare gas. Since the rare gases are expected to dissolve as neutral atoms (promotional energies to p^5s configuration range from 156 kcal/mole for Rn to 383 kcal/mole for Ne) these thermodynamic data may be used to estimate the magnitude of interaction energies between neutral atoms and metal ions when the latter are part of a metallic structure. Such information will aid in the development of a theory of metallic solutions.

To experimentally determine the very low solubilities of the rare gases in liquid alkali metals a large quantity (~3.2 liters) of the liquid alkali metal was saturated by circulation of the rare gas through the liquid metal. A large sample (1 to 2 liters) of the saturated liquid metal was analyzed for the rare gas. Precautions were taken to avoid contamination of the sample with the surface layer of the saturated liquid since the quantity of adsorbed gas may be many times greater than the dissolved gas. The dissolved rare gas was stripped from the sample by sparging with helium. The rare gas was separated from the helium stream by adsorption on liquid nitrogen cooled charcoal. After desorbing from the charcoal the rare gas was measured either by mass spectrometric or radiochemical methods.

The solubility of argon and krypton in liquid sodium has been measured. The solubility of argon ranges from 2×10^{-10} to 3×10^{-9}atom fraction over the temperature range 340-480°C at one atmosphere argon pressure. The solubility of krypton ranges from 2×10^{-12} to 1.2×10^{-9} atom fraction over the temperature range 200-480°C. The heat of solution for both gases in liquid sodium is approximately 16 kcal/mole. The heat of solution may be shown to be equal to the sum of two parts, the energy to make a cavity in the body of the solvent and the interaction energy between the solute and solvent atoms. Calculated and observed heats of solution are equal if the cavity radius is taken to be about 70% greater than the atomic radius of the rare gas atoms.

During the next year the solubility of krypton in the other alkali metals will be measured.

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

H. M. Feder/I. Johnson/F. Cafasso/V. Khanna March 13, 1964

THERMODYNAMICS - BINARY ALKALI METAL SOLUTIONS

Recent theoretical advances have been made in the area of metallic solutions.[1] Great promise exists for the future development of a theory which will make possible theoretical calculations of the thermodynamic properties of simple metallic solutions. The binary alkali metals form such simple solutions. A study designed to measure the thermodynamic properties of selected binary liquid alloys formed by the alkali metals was undertaken to provide experimental data for comparison with future theory.

The high chemical reactivity and chemical similarity of the alkali metals limits the possible experimental methods which may be used to determine thermodynamic activity. Where multiple species exist in a vapor phase, as in the case of the alkali metals, a vapor pressure method may be used provided that it is possible to determine the partial pressures of the different species independently. The optical absorption method used in this study permits the concentration of the atoms in the vapor to be distinguished from that of the molecules. In this technique the partial pressure of alkali atoms is determined by measuring the quantity of light of certain characteristics (resonance radiation) absorbed by the vapor. Comparison of the absorption by vapor over an alloy with that over the pure metal is a direct measure of the thermodynamic activity of one of the components in the binary solution.

The sodium-potassium system is the first binary to be studied. The absorption of the 5890 A line of the Na doublet by vapor over pure liquid Na was measured from 127.7 to 152.7°C. The enthalpy of vaporization for the reaction $Na_{(l)} \rightleftarrows Na_{(g)}$ calculated from the temperature dependence of absorption is 25.6 kcal/mole. The best literature value for this enthalpy[2] is 24.9 kcal at 150°C.

Five compositions (10% Na-90% K; 22% Na-78% K; 44% Na-56% K; 56% Na-55% K; and 74% Na-26% K) will be examined over the temperature range in which measurable absorption occurs. The activity coefficient of both components, Na and K, will be determined experimentally for each composition.

---

[1] A. Bellemans and M. DeLeener, Phys. Rev. Letters, 6, 603 (1961); Phys. Letters, 4, 157 (1963).

[2] M. Sittig, "Sodium, Its Manufacture, Properties and Uses," Reinhold Publishing Corp., New York, N. Y. (1956).

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

I. Johnson/M. G. Chasanov

March 13, 1964

THERMODYNAMICS OF LIQUID METAL SOLUTIONS

The realization that liquid metal solvents are very useful for the processing of nuclear materials has led to the need for thermodynamic data on a large number of systems. Previous thermodynamic studies of liquid metal solutions have largely been confined to the mixtures of the more common low melting metals. In the present studies thermodynamic data on systems of potential use to the nuclear energy program are being obtained. These data are also extending our knowledge of the behavior of more complex metallic systems and therefore will be of use in judging the relative importance of those factors which are necessarily omitted in the initial development of theory.

High temperature galvanic cells are being used to obtain data on the thermodynamic properties of metallic solutions and of the solid metallic phases in equilibrium with these solutions. A systematic study has been completed on the binary systems of uranium with the low melting metals zinc, cadmium, gallium, indium, thallium, tin and lead.[1] A similar study of the binary systems of plutonium with low melting metals has been started; the systems Pu-Zn and Pu-Cd have been completed. A study of the thermodynamics of the binary systems of the rare-earth metals with cadmium has been started. The systems La-Cd, Ce-Cd and Pr-Cd have been completed. All of the systems thus far examined have well defined intermetallic compounds which the thermodynamic studies have shown to have large exothermic heats of formation. The thermodynamic stability of compounds with a given metal, as measured by the free energies of formation, increase in the order uranium, plutonium, rare-earth metals. Plutonium appears to be more like a rare-earth metal than does uranium. The actinide and rare-earth metals in the low melting solvent metals generally have large negative excess partial molar free energies. In a common solvent system the deviations from ideal behavior increase in the order: uranium, plutonium, rare-earth metals. Again plutonium behaves more like a rare-earth metal than does uranium.

It is planned to continue the studies already underway on systems containing rare-earth metals or plutonium.

---

[1] Proc. of Symposium on the Thermodynamics of Nuclear Materials, IAEA, Vienna 1962, p. 319; Trans. Met. Soc. AIME **224**, 468 (1962).

2B4

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

I. Johnson/E. Veleckis March 13, 1964

PHASE STUDIES BY THE EFFUSION METHOD

The rare-earth metals are known to form complex series of intermetallic phases with the low melting B-subgroup metals. These intermetallic phases offer an unparalleled opportunity to study the variation in stoichiometry, thermodynamic stability and structure with atomic size uncomplicated by changes in electronic configuration. Thus, as one progresses from the light to the heavy rare-earth metals electrons are added to the 4f orbitals, without changing the number of valence (or conductance) electrons except at europium and ytterbium where the enhanced stability of the half-filled and completely filled 4f levels causes a transfer of electrons from the valence shell to the 4f shell. The buildup of the nuclear charge which accompanies this electron addition causes the effective radius to smoothly decrease (with the exception of europium and ytterbium); the mean metallic radius decreasing from 1.877 Å for lanthanum to 1.734 Å for lutetium.

The stoichiometry, relative stability and structure of the binary phases formed between the rare-earth metals and a relatively volatile B-subgroup metal is being studied using a continuous weighing effusion method supplemented by X-ray diffraction studies. The effusion method permits the stoichiometry and the approximate thermodynamic stability of the various phases to be determined. The X-ray diffraction studies yields the structures of the complex series of phases as well as their atomic parameters. The binary systems of the four light rare-earth metals (lanthanum, cerium, praseodymium and neodymium) with zinc and cadmium have been studied. Preliminary data indicate that the stability of a compound with a given structure decreases as the radius of the rare-earth metal decreases and that the stability of compounds between a given rare-earth metal and either zinc or cadmium increases with decreasing zinc (or cadmium) to rare-earth metal ratio reaching a maximum stability at the RE Zn$_2$ or RE Cd$_2$ compound. The 1:1 compound is less stable in all cases. The change in stability with increasing atomic number of the rare-earth metal leads to fewer different intermetallic phases for the heavier rare-earth metal-zinc (or -cadmium) systems.

These studies will be continued during the next year; the systematics of the heavier rare-earth metals will be established.

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

H. M. Feder/F. Cafasso/D. M. Gruen*/C. Thalmayer*

March 13, 1964

MAGNETIC SUSCEPTIBILITY STUDIES

Uranium monosulfide (US) is one of four uranium alloys known to undergo a ferromagnetic transition. In order to learn more about the electronic configuration of uranium in magnetically-concentrated alloys of this kind, the magnetic susceptibility of US and US-ThS solid solutions are being measured.

Magnetic susceptibility measurements are made by the Faraday method. Samples contained in 4 mm O.D. quartz capsules are suspended from one arm of a microbalance by a cupronickel chain. The suspension extends into a metal cryostat the lower end of which terminates between two isodynamic gap-type pole pieces.

The assessment of the electronic configuration of a magnetic atom depends largely upon a comparison of its measured moment with theoretical moments. Theoretical moments are calculated for atoms free from exchange and/or crystal field interactions. The measured moments, however, are effected by both types of interactions. The ferromagnetism shown by US[1] indicates the exchange interactions are strong in this compound. By alloying US with the isomorphous diamagnetic compound ThS (i.e., by magnetic-dilution), it may be possible to reduce this interaction to such an extent that the compound's ferromagnetism may be lost and theoretical behavior nearly approximated. From magnetic measurements made over a composition range (100% US to 100% ThS) of US-ThS solid solutions, the magnetic moment of US at infinite dilution will be found by extrapolation. This extrapolated moment will be compared with theory.

---

* Chemistry Division

[1] W. Trzebiatowski and W. Suski, Roczn. Chem., 37, 117 (1963).

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

C. E. Crouthamel/C. E. Johnson/R. Heinrich

March 13, 1964

LITHIUM HYDRIDE REGENERATIVE CELL

The formation of lithium hydride can be accomplished in a reversible manner in an emf cell by the oxidation of liquid lithium metal (the anode) and the reduction of hydrogen gas diffusing through a metal diaphragm (the cathode). The cell product, lithium hydride, distributes between the cell electrolyte and the liquid lithium metal anode. By cycling either of the liquid phases containing the lithium hydride to a high temperature, the cell reactants (liquid lithium and hydrogen) may be regenerated, separated and returned to their respective anode and cathode compartments.

Data are being obtained by analysis of heating and cooling curves of the solid-liquid equilibrium of fused lithium salt systems; emf-temperature-composition data for the lithium hydride cell are also being obtained; and the permeation rates of hydrogen through metal diaphragms have been determined. Thermal analysis investigations of the solid-liquid equilibria on the binary systems LiCl-LiH, LiBr-LiH, and NaCl-LiH are completed. The ternary phase diagram LiF-LiCl-LiH is being obtained, and the region of the ternary eutectic would be the most probable electrolyte composition of a hydride cell.

Emf-temperature-composition studies on the lithium hydride cell are in progress. Measurements of the standard free energy of formation of lithium hydride and of the activity of lithium hydride in the various electrolytes will continue.

Recent Publications

1. C. E. Johnson, S. E. Wood, and C. E. Crouthamel, "Anomalous and Non-Equilibrium Breaks in Fused Salt Thermal Analysis Curves," Nature 201, 293 (1964).

2. C. E. Johnson, S. E. Wood, and C. E. Crouthamel, "Studies of LiH Systems," Inorganic Division, ACS, April (1964).

3. U. S. Patent No. 3,119,723, January 28, 1964, C. E. Crouthamel and M. S. Foster (Iron H_2, H^- Diaphragm Electrode).

4. U. S. Patent Applied for, March 1964, C. E. Crouthamel, R. Heinrich and C. E. Johnson (Vanadium H_2, H^- Diaphragm Electrode).

2B7

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

C. E. Crouthamel/M. S. Foster March 13, 1964

BIMETALLIC REGENERATIVE CELLS

The bimetallic regenerative cell is composed of a liquid alkali metal anode, a fused salt electrolyte containing the alkali metal ion and a liquid cathode metal. The cell process is the oxidation of the anode metal to produce alkali metal ions in the electrolyte and at the cathode the alkali metal ions are reduced to metal and diffuse into the liquid metal cathode. By cycling the liquid cathode metal to a high temperature, the alkali metals may be vaporized from selected cathode metals (e.g., Sn, Bi, Pb) and returned to the anode.

Very little is known about the thermodynamic properties of these binary alloy systems over the temperature ranges of interest. Also, phase diagram (solid-liquid equilibrium) data for many of the fused salts systems which would be applicable to these cells are not available.

Emf-temperature-composition data on the lithium-bismuth and lithium-tin alloys have been completed and the data for sodium-bismuth alloys are partly completed. Also, the mass spectrographic analysis of the vapor phase (Knudsen Cell) for the lithium-bismuth system has been completed. Demonstration experiments of regeneration of the cathodic alloy by the isopiestic method have been made for Li-Bi, Na-Bi, Li-Sn and Na-Sn alloys.

Future work will extend the emf-temperature-composition data for the sodium-bismuth cell, and also the data for the vapor pressure and vapor phase species in equilibrium with the alloys produced in the regenerative cells. Investigations of the phase diagrams for fused salt electrolytes applicable to the sodium-bismuth cell will be initiated; electrolytes of interest are NaX ($X = F^-, Cl^-, Br^-, I^-$), NaCn and possibly NaOH.

Recent Publications

Melvin S. Foster, Scott E. Wood, and C. E. Crouthamel, "Thermodynamics of Binary Alloys, The Lithium-Bismuth System," Inorganic Division, ACS, April (1964).

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

C. E. Crouthamel/M. S. Foster March 13, 1964

SOLUBILITY OF INTERMETALLIC COMPOUNDS IN FUSED SALTS

During the past year, the solubility of many intermetallic species in fused salt media was observed for the first time! This discovery was made in the course of bimetallic cell studies when the irreversible transfer of cathodic metal to the anode was noted. Also, red, green, and yellow colorations of the electrolytes were observed; these observations could not be attributed to alkali metal solubility.

The design of regenerative bimetallic cells for the direct conversion of heat into electricity will have to take into account the possible irreversible transfer of both anodic and cathodic metals through the electrolyte. The solubility of intermetallic species in the fused salts now establishes an irreversible process for the transfer of cathodic metal in the cell. Previously the solubility of the free alkali metal in the fused salt was considered the only irreversible process for the transfer of metal in the cell.

Quantitative measurements of lithium-bismuth intermetallic solubility in fused salts have been made, and the results indicate that two species, Li_3Bi and LiBi both dissolve in the lithium chloride-lithium fluoride fused salts. The fused salts saturated with intermetallic compounds of Li_3Bi, Li_2Te and Na_2Te have been scanned in the heated sample chamber of a Cary 14H spectrophotometer, and it was observed that these systems are characterized by a broad absorption peak in the visible region. These studies and solubility measurements are currently in progress. The phenomena of solubility of intermetallic compounds in fused salts appears to extend over a wide range of alkali and alkaline earth intermetallic species with a variety of cathodic metals, e.g., Bi, Sn, Cd, Pb, Te, Se, etc.

The work for the current year will be continued next year with the expansion of the spectrophotometric and solubility studies. The effect of this phenomena on bimetallic cell operation does not appear to be serious at cell operating temperatures; however, a more complete evaluation will be made as more data become available during the coming year. Efforts will also be made to elucidate the properties of the intermetallic species in fused salts. The experiments require extremely pure inert atmosphere boxes and are difficult and time-consuming to execute.

Recent Publications

1. M. S. Foster, C. E. Crouthamel, D. M. Gruen and R. L. McBeth, First Observation of a Solution of Li_3Bi, an Intermetallic in Molten LiCl-LiF, J. Phys. Chem., (in press), April 1964.

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

C. E. Crouthamel/J. Elder

March 13, 1964

REGENERATIVE CELL KINETICS

For power applications, regenerative cells must be designed with the capabilities of functioning at high electrode current densities (e.g., 100 to 1000 ma/cm^2) and at about one-half or more of the open circuit voltage.

Experiments have demonstrated that most of the bimetallic systems are in fact capable of these high current densities and voltage outputs. However, the systems cannot be optimized with respect to overall power density and operating characteristics without a more detailed knowledge of the electrode kinetics.

An understanding of the causes of any slow step in the overall electrode process, prior to, during, or after the charge transfer process, requires a study of the current voltage relationships under a variety of experimental conditions. These experimental conditions can be arranged so that either charge transfer or mass transfer phenomena govern the results. To preclude mass transfer effects, a pulse electrolysis technique will be employed. The data from normal electrolysis will be characteristic of mass transport phenomena. In both methods, constant current (galvanostatic) and constant voltage (potentiostatic) techniques will be applied. Because of the extreme chemical reactivity of the bimetallic and hydride cells, all experiments will be carried out in high purity inert-atmosphere boxes.

The potentiostatic and galvanostatic equipment have been installed in conjunction with an inert atmosphere box during the past year. Various cell designs have been considered; those for mass transport studies are under construction and those for pulse electrolysis are still in the design stage.

The experimental program will begin in the next year with mass transport experiments on the sodium-bismuth bimetallic cell and the lithium hydride cell. This will be followed by the pulse electrolysis studies on the same systems as soon as suitable cells can be constructed.

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

W. N. Hubbard/G. K. Johnson/E. Greenberg March 13, 1964

THE ENTHALPIES OF FORMATION OF THE DIBORIDES OF SOME GROUP IV AND V METALS

The diborides of the Group IV and V metals are potential materials of construction for high temperature applications. Whatever sparse thermochemical data exist are uncertain because both bomb calorimetric and equilibrium vapor pressure studies involve reactions difficult to define. Fluorine bomb calorimetry, on the other hand, leads to well-defined products of combustion. Already enthalpy of formation data have been determined for many of the products of formation, the tetrafluorides of titanium[1], zirconium[2], and hafnium[1], the pentafluorides of niobium and tantalum (unpublished), and the trifluoride of boron[3]. In this program the enthalpies of formation of the diborides of zirconium, hafnium, and niobium have been determined by fluorine bomb calorimetry (unpublished). A two-compartment reaction vessel[4] was used in which it is possible to maintain the fluorine in a separate compartment from the sample until intentional ignition was desired.

It is planned to obtain the enthalpies of formation of the diborides of titanium and tantalum.

Publications

1. "Fluorine Bomb Calorimetry. IV. The Heats of Formation of Titanium and Hafnium Tetrafluorides," E. Greenberg, J. L. Settle, and W. N. Hubbard, J. Phys. Chem. 66, 1345 (1962).

2. "Fluorine Bomb Calorimetry. I. The Heat of Formation of Zirconium Tetrafluoride," E. Greenberg, J. L. Settle, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 65, 1168 (1961).

3. "Fluorine Bomb Calorimetry. III. The Heat of Formation of Boron Trifluoride," S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 65, 2157 (1961).

4. "Combustion Bomb Reaction Vessel for Spontaneously Combustible Materials," R. L. Nuttall, S. S. Wise and W. N. Hubbard, Rev. Sci. Inst. 32, 1402 (1961).

ARGONNE NATIONAL LABORATORY — Chemical Engineering Division

W. N. Hubbard/E. Greenberg

March 13, 1964

THE ENTHALPIES OF FORMATION OF SILICON CARBIDE AND TETRAFLUOROMETHANE

The literature values for the enthalpy of formation of silicon carbide range over 8 kcal/mole.[1] Because the combustion in oxygen is very difficult to carry out, a determination is being carried out by combustion of silicon carbide in fluorine in a bomb calorimeter. In oxygen bomb work on which the current "selected best value" is based, most of the heat evolved was from combustion of a kindler, titanium, used to promote combustion. Silicon carbide, however, burns quite readily in fluorine. Combustions are being carried out with both alpha and beta forms.

The value of the enthalpy of formation of silicon carbide obtained will depend on values of the enthalpies of formation of the product fluorides, the tetrafluoride of silicon and carbon. A value for the former has already been determined.[1] The best literature values for tetrafluoromethane range over 3 kcal/mole.[2] Attempts will be made to obtain a better value by combustion of carbon, either graphite or diamond, in fluorine. In principle this method should yield the best possible value, as the measured heat is itself the heat of formation.

Publications

1. "Fluorine Bomb Calorimetry. V. The Heats of Formation of Silicon Tetrafluoride and Silica," S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 67, 815 (1963).

2. "The Application of Fluorine Bomb Calorimetry to the Solution of Some Persistent Problems in Light Element Thermochemistry," W. N. Hubbard, H. M. Feder, E. Greenberg, J. L. Margrave, E. Rudzitis and S. S. Wise. Presented at the Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July (1963).

2B12

ARGONNE NATIONAL LABORATORY　　Chemical Engineering Division

W. N. Hubbard/J. L. Settle　　March 13, 1964

THE ENTHALPIES OF FORMATION OF URANIUM COMPOUNDS

Considerable uncertainty exists in the thermochemistry of uranium compounds because of both the difficulty of the preparation of adequately characterized samples for study, and the difficulty of devising suitable calorimetric reactions. Considerable effort has been spent to obtain well-characterized samples. Combustion of the sample in fluorine in a calorimeter is being tried as a general method for the enthalpy of formation determinations.

Fluorine bomb calorimetry has already proved a useful tool[1] in this laboratory for the study of difficult compounds. The enthalpy of formation of uranium hexafluoride has been determined[2] as a datum necessary to the general application of fluorine reaction calorimetry to uranium compounds.

Many of the uranium compounds are fluorine sensitive and must be protected from fluorine before intentional ignition is desired. One promising technique that is being studied involves the use of flow calorimetry rather than bomb calorimetry. Fluorine is not introduced into the calorimeter until intentional ignition is desired. If the technique proves satisfactory, a flow calorimeter will be constructed. The first compounds studied will probably be the sulfides and phosphides of uranium.

Publications

1. "Fluorine Bomb Calorimetry. V. The Heats of Formation of Silicon Tetrafluoride and Silica," S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 67, 815 (1963).

2. "Fluorine Bomb Calorimetry. VI. The Enthalpy of Formation of Uranium Hexafluoride," J. L. Settle, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 67, 1892 (1963).

2B13

ARGONNE NATIONAL LABORATORY Chemical Engineering Division

W. N. Hubbard/D. R. Fredrickson/A. Hu/J. E. Brugger March 13, 1964

THE DESIGN AND CONSTRUCTION OF A 1500°C HIGH PRECISION ENTHALPY INCREMENT DROP CALORIMETER

High temperature enthalpy data are unavailable for many compounds of interest in high temperature chemistry. As actual measurement is the only satisfactory means of obtaining these data for condensed phases, a program has been initiated to design and construct a calorimeter for obtaining precise high temperature enthalpy data. The equipment has been designed and the component parts are undergoing testing.

The calorimeter is of the drop type and consists of a drop mechanism which rests on a furnace in which the sample is suspended, a gate through which the sample falls, and a calorimeter in which the heat evolved by the sample is measured. Subassemblies of these four parts have been tested. Improvements are being made where necessary. During the next year the complete assembly will be tested and calorimetric measurements started unless unforeseen problems arise.

Initial measurements will include studies with synthetic sapphire, using the NBS standard sample. Studies may also be made with molybdenum, tungsten and tantalum and some of the compounds for which room temperature heats of formation have been determined in this laboratory.

SECTION 3A

BROOKHAVEN NATIONAL LABORATORY - CHEMISTRY DEPARTMENT

3A1 Nuclear Chemistry - Nuclear Reactions

3A2 Nuclear Chemistry - Nuclear Spectroscopy

3A3 Nuclear Chemistry - Nuclear Geochemistry

3A4 Solar Neutrinos

3A5 Radiation Chemistry

3A6 Hot Atom Chemistry

3A7 Isotope Effects

3A8 Physical Chemistry - Inorganic Reactions in Solution

3A9 Physical Chemistry-Theoretical Organic Chemistry

3A10 Physical Chemistry--Molecular Excitation and Reactions in the Gas Phase

3A11 Physical Chemistry--Biochemical Processes

3A12 Molecular and Crystal Structure

3A13 Analytical Chemistry

For further information on work completed, the reader is referred to the open scientific literature and to the Brookhaven National Laboratory Annual Report, July 1, 1964. The report number is BNL 867 (AS-18). Publication is expected by November, 1964.

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

G. Friedlander/S. Katcoff/M. Perlman/J. Cumming 5/1/64
J. R. Grover/N. Porile/A. Poskanzer/R. W. Stoenner

NUCLEAR CHEMISTRY - NUCLEAR REACTIONS

Nuclear reaction studies are carried out with various projectiles (protons, deuterons, helium ions, pions, etc.) impinging on complex ($Z \gtrsim 2$) nuclei. Particle beams from the various accelerators at the Laboratory (60-inch cyclotron, Cosmotron, AGS) are used in this work, so that an energy range from a few MeV to 30 GeV is being spanned. The principal emphasis has been on the energy regions accessible with the Cosmotron and AGS, but studies at lower bombarding energies are often used to complement the high-energy work. By far the greatest volume of research has been done on proton-induced reactions; however, with increasing beam intensitites, the use of secondary particles such as pions and antiprotons for reaction studies is becoming more feasible and will be of great interest in the future.

The principal aims of the high-energy reaction studies are (1) information on the systematics of the very complex patterns of reactions observed, i.e., knowledge of how the cross section for formation of any particular product depends on bombarding particle, on bombarding energy, and on mass and atomic number of target nucleus; (2) an understanding of the reactions in terms of mechanisms and models. Additional goals of at least some of the reaction studies are, on the one hand, to correlate the behavior of complex nuclei under high-energy bombardment with interactions between elementary particles and, on the other hand, to obtain information on the structure of atomic nuclei.

A variety of techniques is used in the study of interactions of high-energy particles with complex nuclei. Those reaction products which are radioactive are most often identified and measured by means of their characteristic decay properties. To obtain cross sections by this method, one must know in some detail the radiation properties of the nuclide in question and, for this reason, certain nuclear spectroscopy investigations are natural adjuncts of reaction studies. A complementary and potentially very powerful technique for determination of the relative yields of reaction products involves mass-spectrometric detection. The development of the requisite high-sensitivity mass spectrometry and of rather specialized ultra-microchemical source preparation methods are therefore being actively pursued.

From knowledge of reaction cross sections alone, it is usually not possible to deduce reaction mechanisms. Greater insight into the details of reactions can be obtained if, in addition, there is information about the energy and momentum transferred to the reaction products. Such information comes from experiments on the angular and energy distributions of reaction products recoiling out of extremely thin targets. Experiments of this type are therefore receiving increasing emphasis. Additional details about reactions are obtained from observations of the various charged particles (recoil nuclei, fragments, α particles, protons, mesons) in nuclear emulsions and in bubble chambers.

The detailed interpretation of high-energy reactions in terms of mechanisms usually involves comparison of experimental results with calculations based on certain models, and these calculations are so complex as to require extensive use of high-speed computers. In particular, Monte Carlo methods have been found very useful in this work.

Investigations of spallation, fission, and fragmentation processes will be carried out at both the Cosmotron and AGS. It is anticipated that detailed recoil studies of the Cu^{65} (p,pn) reaction will be completed. Completion and analysis of the differential recoil experiment on neutron-excess and neutron-deficient fission products of uranium bombarded with 3-GeV protons is expected to yield significant information on the time scale of the fission processes leading to these products. A new experiment will be undertaken in an external proton beam at the Cosmotron to study the energy spectra of and angular correlation between fission fragments produced in high-energy fission of uranium. The reaction Au^{197} (p,spallation)Tb^{149}, which is widely used as a monitor reaction for high-energy proton beams, is being reinvestigated and the excitation function is being extended to AGS energies; this study will be completed. The spark source mass spectrometer will be used in attempts to obtain mass-yield data for rare-earth products formed in uranium targets irradiated in the AGS.

Further intensive efforts towards elucidating fragmentation processes are expected. These will include analysis of the detailed studies of the cross sections for formation of the delayed-neutron emitters Li^9, C^{16}, and N^{17} from many targets; further experiments on delayed-proton emitters; and exploitation of the recently developed techniques for measuring yields of short-lived rare gas products. A nuclear-emulsion investigation of the energy spectra of Li^8 fragments ejected from Cu and Ag targets at various angles will be brought to a conclusion.

Further progress is expected in the extension of Monte Carlo cascade calculations to higher energies and in their application to the interpretation of experimental results.

NUCLEAR CHEMISTRY - NUCLEAR REACTIONS

(continued)

Publications

1. Porile and Tanaka, "Nuclear Structure Effects in High-Energy (p,pn) Reactions", Phys. Rev. 130, 1541-48 (1963).

2. Fraenkel, "Pion Capture in Complex Nuclei", Phys. Rev. 130, 2407=16 (1963).

3. Porile and Tanaka, "The (p,pxn) Reactions of Br^{79} and Br^{81} with 2.9-GeV Protons", Phys. Rev. 132, 397-400 (1963).

4. Cumming, "Absolute Cross Section for the $C^{12}(p,pn)C^{11}$ Reaction at 50 MeV", Nuclear Phys. 49, 417-423 (1963).

5. Cumming, "Monitor Reactions for High Energy Proton Beams", Ann. Rev. Nucl. Sci. 13, 261-86 (1963).

6. Foreman, "Excitation Functions for the (p,pn) and (p,2p) Reactions on Ce^{142}, 0.37 to 2.85 GeV", Phys. Rev. 1768-70 (1963).

7. Thomas and Vandenbosch, "Correlation of Fission-Fragment Kinetic-Energy Fine Structure with a Semi-Empirical Mass Surface", Phys. Rev. 133, B976-82 (1964).

8. Donovan, Mollenauer and Warburton, "Inelastic Scattering of 10.2-Mev Protons by N^{14}", Phys. Rev. 133, B113-16 (1964).

9. Porile and Church, "Isobaric Yield Distributions in the Interaction of 1.8-GeV Protons with Zr^{96}, Mo^{96} and Ru^{96}", Phys. Rev. 133, B310-17 (1964).

10. Schwarzschild, Poskanzer, Emergy and Goldhaber, "Another Search for H^5", Phys. Rev. 133, B1-2 (1964).

11. Cumming, Cross, Hudis and Poskanzer, "Study of a Fragmentation Reaction by Thin-Target Recoil Techniques. The Production of Na^{24} from Bismuth by 2.9-GeV Protons", Phys. Rev. 134, B167-74 (1964).

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

M. L. Perlman/W. Rubinson/S. Katcoff 5/1/64

NUCLEAR CHEMISTRY - NUCLEAR SPECTROSCOPY

Nuclear spectroscopy is the study, in detail, of the radiations emitted by radioactive atoms. These radiations include alpha, beta, and gamma rays emitted directly from the nucleus, and the conversion electrons, Auger electrons, and x-rays emitted from the orbital electrons. Analysis of the results gives information about the structure of nuclei in various states of excitation. Some of the excited states have properties describable as excitation of only one or of a few nucleons, with the remainder of the nucleus being essentially unaffected. Some excited nuclear states are found to have properties which correspond to energy stored in the nucleus as a whole, such as in vibrations or rotations or both. The properties of still other states seem to be the result of a coupling between particle and collective excitation. This latter aspect is of special interest in the current research.

The interaction of nuclear transitions with the orbital electrons of an atom has been of interest by itself. This study is related to atomic structure as well as to nuclear structure.

A substantial portion of the research in nuclear spectroscopy is associated with studies of nuclear reactions. It is often necessary to study the radiations of certain nuclides in order to measure their yields reliably from various nuclear reactions.

In addition to a continuing investigation of rotational and vibrational levels of deformed nuclei, two new investigations are being started. The first is a study of the x-ray and Auger electron spectra produced in spontaneous fission. This should provide information on the primary atomic number distribution for various mass splits. Possibly, something will also be learned about how the atomic electrons rearrange as the single heavy nucleus divides in two. The second new investigation is a study of M x-ray fluorescence yields in the heavy element region by L-M x-ray coincidence measurements with proportional counters. M shell fluorescence yields are now very poorly known, but they are needed to interpret unambiguously some observations on the Pb M x-ray spectrum that is emitted in the process of Po^{210} decay.

Research with the double focusing beta-ray spectrometer will be greatly facilitated by use of the new mass separator to prepare pure, thin, "weightless" sources. High resolution "beta-ray" spectrometry depends strongly on source quality.

NUCLEAR CHEMISTRY - NUCLEAR SPECTROSCOPY

(continued)

Publications

1. Chu, Kistner, Li, Monaro and Perlman, "E2/M1 Ratios in the Isomeric Transitions of Te^{121} and Te^{123}, and the Decay of the Te^{121} Isomers to Sb^{121}", Phys. Rev. 133, B1361-67 (1964).

2. Craseman, Emery, Kane and Perlman, "Properties of Radioactive Re^{189}", Phys. Rev. 132, 1681-90 (1963).

3. Dostrovsky, Katcoff and Stoenner, "Half-lives of ^{83}Y and ^{83}Sr", J. Inorg. Nucl. Chem. 26, 209-11 (1964).

4. Dostrovsky, Katcoff and Stoenner, "Decay of Y^{85} Isomers", Phys. Rev. 132, 2600-6 (1963).

3A3

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

O. A. Schaeffer/R. Davis 5/1/64

NUCLEAR CHEMISTRY - NUCLEAR GEOCHEMISTRY

The earth and space chemistry research is directed toward an understanding of the past history of the earth, the solar system and cosmic rays by the use of radioactivity and from the variations in stable isotope abundances. The products of nuclear spallation reactions of cosmic rays are studied in the earth's crust, in meteorites, and in artificial satellites. From a comparison with the nuclear spallation products of high energy accelerator produced protons, new information is obtained about the past history of the meteorites as well as of cosmic rays. From the study of nuclear spallation products in recovered artificial satellites, the cosmic ray intensity near the earth is investigated. Study of these same isotopes in ocean cores, polar snow and atmospheric dust is directed toward understanding cosmic dust accretion of the earth as well as the origin of the cosmic dust itself. Methods of isotopic age dating are developed, improved and extended to solve special problems of interest to earth and meteorite history. In particular, K-Ar dating is applied to very young and very old minerals, the disequilibrium in uranium decay chains, especially U-234 excess, and He-U dating are applied to the chronology of the ice ages. Special problems of archaeological interest are also investigated. Experimentally the investigations are carried out by high sensitivity mass spectrometry, low level counting, activation analysis and electron micro-beam probe analysis. The proton beams of the Cosmotron and the AGS are used to simulate cosmic ray interactions.

It has been found that aragonitic fossil shells and corals usually contain a few ppm of uranium and, in addition, that the He^4 produced by this uranium and daughters is retained in the aragonite lattice for periods of 1 million years and probably for periods of up to 30 million years. This conclusion is based on comparison of He ages with Th^{230}/U^{234} ages on shells and corals less than 3×10^5 years old and by comparison with age estimates based on stratographic position for corals up to 30 million years old. Thus it appears that the He method probably is a practical geochronometer for the direct dating of fossils. This work was done in collaboration with the Lamont Geological Observatory (Columbia University) which provided the Th^{230}/U^{234} age control.

NUCLEAR CHEMISTRY - NUCLEAR GEOCHEMISTRY

(continued)

The He-U dating program for gastropods and corals will be continued to test its applicability to other fossils, to investigate the extent of helium retention in time, and to start critical time measurements.

During the coming year we will complete an investigation of the variation in isotopic composition of lead from ancient mining sites in the Mediterranean region and in England. In addition to the study of lead ore samples, we will examine groups of lead-bearing artifacts from several important archaeologic sites, to help determine the source of the lead, and in particular to look for changes with time in the source of lead at a given locality. These isotopic studies should complement our previous archaeological investigations.

The solid source mass spectrometer has been modified to permit precise measurement of the U^{234}/U^{238} ratio for uranium samples as small as 10 μg. The instrument will be used for a study of uranium disequilibrium in marine sediments and marine carbonate shells. Since work at Columbia has indicated the extreme difficulty of separating "authigenic" uranium from deep sea sediments, we will first explore the uranium isotope ratios in certain continental shelf sediments in which uranium is probably enriched. The small amount of uranium required for the mass spectrometric analysis may also, however, permit significant studies on certain types of deep sea sediments.

It is planned to extend the Ar^{39} and rare gas measurements to the rarer types of meteorites, such as the iron meteorites which are already known to have exposure ages on the order of hundreds of millions of years. Also, other radioactivities will be looked at, such as Cl^{36} and Al^{26}. This will serve to check the exposure ages based on Ar^{39}, and also, since the half lives of these nuclides vary from 270 years to 750,000 years, will enable an estimate to be made as to whether the cosmic ray intensity has varied over that period of time.

A continuing effort over the past several years is to obtain specimens of meteorites which have recently fallen. This permits nuclides of a rather short half life to be measured. Some examples are: 35-day Ar^{37}, 310-day Mn^{54}, 2.2-year Na^{22}, and 5-year Co^{60}.

NUCLEAR CHEMISTRY - NUCLEAR GEOCHEMISTRY

(continued)

We plan to continue the investigation on recent meteorite falls in order to improve the measurement of the spatial gradient, both with new meteorite falls and improving the cross section measurements. In particular $\mathrm{Ar}^{37}/\mathrm{Ar}^{39}$ ratio measurements as a function of energy are planned to test the effect of energy variation of this ratio on the meteorite measurements.

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

R. Davis, Jr./D. S. Harmer 5/1/64

SOLAR NEUTRINOS

The fusion reactions in the sun produce neutrinos which leave the sun with little absorption or energy loss. These particles serve as a direct signal from the center of the sun that carries detailed information on the solar energy generation process. This approach to the study of solar energy generation has not as yet been explored, since detection systems with sufficient sensitivity have not been developed. An exploratory experiment along these lines must be guided by the results of calculations of solar neutrino fluxes. Sears, Bahcall and Fowler have recently investigated the solar model calculations and the relevant nuclear reaction data to deduce the neutrino flux and have also evaluated the possible errors associated with these calculations. The neutrino producing reactions and the flux at the earth presented by this group is as follows: $H(H,e^+\nu)D$, $\phi = 5.8 \times 10^{10}$; $Be^7(e^-,\nu)Li^7$, $\phi = 0.8 \times 10^{10}$; and $Be^8 \rightarrow Be^{8*} + e^+ + \nu$, $\phi = 1.9 \times 10^7$ cm^{-2} sec^{-1}. These fluxes are considered to be in error by at most a factor of two.

A pilot experiment was performed in an attempt to observe solar neutrinos by a method based on the reaction Cl^{37} $(\nu,e^-)Ar^{37}$ to form the 35-day radioactive Ar^{37}. The experiment used 1000 gallons of perchlorethylene, C_2Cl_4, and as a target and the irradiation was carried out in a mine 2300 feet deep. A mine is chosen as an irradiation area to shield the target from cosmic rays. This experiment served to set a limit on the solar neutrino flux, which was a factor of 8 above the calculated flux. The limit set was of value in eliminating from consideration certain reactions postulated in the past as contributors in the solar energy generation process. The performance of this small scale experiment showed that the method could be extended in sensitivity sufficient to measure the calculated solar flux, and that background effects from cosmic radiation and local radioactivities could be reduced to a factor of 100 below the calculated neutrino signal.

To measure the calculated solar flux requires an improvement in sensitivity of one-hundred. Since we have developed a counter having an essentially zero background, the remaining way of improving the sensitivity by the Cl^{37} -Ar^{37} method is to increase the volume of perchlorethylene. A full scale experiment is planned that would use 100,000 gallons. To insure complete elimination of cosmic ray background effects the tank of liquid must be located in a mine at least 4000 feet deep. Two mines in the United States have been located that are suitable for the experiment. The owners

SOLAR NEUTRINOS
(continued)

will provide space in these mines to be used for this purpose. A preliminary design of the tank has been made and the cost of fabricating the tank in the mine has been estimated. Approximately one year would be required to prepare the cavity and to erect the tank in the mine.

The mine owners would prepare a cavity for the tank and provide facilities essential for the experiment. The tank would be erected in place by a subcontract according to specifications set by the BNL engineering staff. The internal system for agitating the liquid and mixing with helium gas used for removing Ar^{37} activity is to be designed by our engineering staff and installed by the vessel contractor. The apparatus for isolating Ar^{37} from the helium gas stream will be fabricated at BNL, tested, and finally moved to the mine as a unit.

The experiment is designed to observe the calculated solr neutrino flux with an error of 10%. On the other hand, if the forecasted flux was overestimated, the apparatus would have sufficient sensitivity to observe a flux as low as one-tenth the present calculated value. After the apparatus is completed and preliminary tests performed, a measurement of the solar neutrino flux would require about one year. If the signal is 10 per day or more, a measurement of the rate at perigee versus apogee of the earth's orbit would be performed to test for the 7% difference in neutrino intensity due to the eccentricity of the earth's orbit. Two years' observation would be necessary to reveal this effect. If these measurements are successful, the solar neutrino flux would be followed with time to test for a possible correlation with the solar surface activity cycle of 11 years. Although such an effect is not expected, measurements would be continued to test for the effect.

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

A. O. Allen/H. A. Schwarz 5/1/64

RADIATION CHEMISTRY

The aim of this work is to characterize and measure the yields of chemical reactions caused by ionizing radiation, and to test theories advanced to explain the observed effects. Systems under study include organic materials as well as pure water and dilute aqueous solutions. Systematic measurements are made with radiations of different types, covering a wide range of radiation quality and intensity. When looked at in detail, reactions produced by ionizing radiation are found to proceed through formation of various short-lived intermediates, many of which may be characterized as free radicals. The properties of such radicals are of interest in many branches of chemistry. There are thus two aspects in the basic study of radiation chemistry: first, the radiation is a convenient source of free radicals and other transient chemical entities, the properties of which are an important field of study in themselves; second, an understanding of how the radiation gives rise to the products found in a chemical system, including the free radicals, constitutes an important field of fundamental chemical studies and supplies basic knowledge required for prediction of radiation effects in technological and biological systems.

The γ-ray decomposition of azoethane adsorbed on the surface of inert mineral solids is being investigated. Azoethane is chosen because formation of nitrogen gas from this compound requires relatively little energy while methane and hydrogen may be formed from states of high eV energy. It is found that considerable decomposition of the organic material occurs by energy taken up from the radiation by the solid and transferred in some way through the solid and then to the organic molecule absorbed on its surface. The results are interpreted in terms of the interaction of excited electronic states of the solid with the organic molecule. It is found that color centers formed by irradiation in silica gel are bleached by simple contact with azoethane. This type of study offers a unique approach to the problem of energy transfer in solids, from solid surface to an adsorbed molecule and in fact to the basic problems of heterogeneous catalysis.

It is planned to extend the work on radiolysis of adsorbed compounds by the use of alkali halides as mineral substrates, since the excited states in these solids are better understood than in the oxide systems hitherto studied. It is hoped that correlations with other types of radiation phenomena in solids can be profitably made.

The number of ions formed by irradiation of a liquid has been determined for the first time by methods which appear to be,

RADIATION CHEMISTRY

(continued)

In principle, straightforward and theoretically unobjectionable. The result is that in hexane, one ion pair is produced per 1200 electron volts of energy given up to the liquid by radiation, regardless of whether the agent producing the ionization is a Compton electron of energy above half a million electron volts, or a conversion electron from dissolved argon-37 having an energy of only 2400 volts. This is only about 2% of the number of ion pairs formed when hexane vapor is irradiated. The yield of ions in carbon tetrachloride is only about 10% greater than that in hexane. Ion yields will be determined in additional liquids and mixtures, the results to provide information on the physical processes underlying the radiation chemistry of liquid systems.

Apparatus has been set up for the spectroscopic study of intermediates of lifetimes down to a few microseconds, using our Van de Graaff electrostatic generator as a source of radiation. Studies have been started on the intermediates formed in radiolysis of oxygenated ferrous sulfate solutions and solutions of electron-capturing substances in organic solvents.

Studies on competitive systems of mixed scavengers in water are being continued in an effort to understand why certain systems seem to indicate a higher yield of solvated electrons produced in neutral water than do other systems. The yield of neutral hydrogen atoms, apparently formed along with the electrons, has been determined in several systems.

A large number of problems still await exploration in the radiation chemistry of water. The effect of radiation quality on the yield of hydrogen atoms in neutral water will be determined and the results should distinguish between the various hypotheses of the origin of these hydrogen atoms. It is also planned to study isotope effects in radiolytic hydrogen formation from water.

Publications

1. Kaufman, "Radiolysis of *n*-butanes", J. Phys. Chem. 67, 671-74 (1963).

2. Czapski and Bielski, "The Formation and Decay of H_2O_3 and HO_2 in Electron Irradiated Aqueous Solutions", J. Phys. Chem. 67, 2180-84 (1963).

3. Allen and Hummel, "Determination of the Number of Separated Ion Pairs Produced in the Irradiation of a Liquid", Faraday Soc. No. 36, 95-101 (1963).

4. Schwarz, "Absolute Rate Constants for Some Hydrogen Atom Reactions in Aqueous Solution", J. Phys. Chem. 67, 2827-30 (1963).

5. Katakis and Allen, "Note: Mechanism of Radiolytic Oxidation of Ferrous Ion", J. Phys. Chem. 68, 657-60 (1964).

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

G. Harbottle/A. P. Wolf 5/1/64

HOT ATOM CHEMISTRY

The field of hot atom chemistry or the chemical effects of nuclear transformations concerns itself primarily with chemical reactions brought about by atoms or molecular fragments having excess kinetic energy. The reactive fragments are frequently electronically excited and the molecular species may also be in vibrationally excited states. The emphasis in research in this field will vary from studies on the nature of the solid state to using recoil fragments for preparing labeled compounds. There are essentially three methods for making hot atoms, in use today: photochemical, acceleration of charged species in devices such as mass separators, and using suitable nuclear reactions. Studies on the nature of the species at birth to investigation of its reactions at near thermal energies encompass the studies being carried out in numerous laboratories.

Part of the research in hot atom chemistry at BNL concerns itself with the reaction of hot carbon and tritium atoms. Previous work has been mainly with carbon-14, but in 1956-57 the group at BNL demonstrated that carbon-11 studies could be carried out conveniently in organic systems by use of appropriate gas-liquid chromatography techniques. The great advantage of low and controllable radiation damage coupled with much greater flexibility in experimental parameters provided an impetus to research in this area. The carbon-11 work, coupled with the demonstration at BNL in 1959 that a high yield of labeled organic product could be found in gas phase recoil work, has made possible fundamental strides in understanding the chemical reactions at high energies.

Various nuclear reactions are used as sources of hot carbon atoms. These include $N^{14}(p,\alpha)C^{11}$ from 10 MeV protons and particularly useful for yield-dose measurements; $C^{12}(n,2n)C^{11}$ with neutrons from a Li target in the cyclotron beam and valuable for studies with hydrocarbons; $C^{12}(p,pn)C^{11}$ from Cosmotron protons, which allow great flexibility and give good absolute yield measurements; $N^{14}(n,p)C^{14}$ from reactor neutrons and primarily useful for preparative studies.

A focal point of our studies has been the "chemistry" of the hot atom reactions subsequent to our demonstration of insertion reactions both with methylene and methyne radicals.

Another phase of hot atom chemistry researches at BNL concerns itself with solids and solutions. In this area the study of processes of recoil atom annealing in solids has led to the bridge between hot atom chemistry and radiation damage. The investigations are carried out with the two-fold purpose of studying high energy chemical reactions and solid state chemistry. For this purpose solution studies are an invaluable adjunct.

Concomitant with, but not subsidiary to, the organic hot atom chemistry, photolytic studies and hot atom labelling reactions are investigated. This work is rounded out by mechanistic studies using tracer techniques.

Work is under way on oxygen dependence of major product yields in C^{11} reactions with alkanes. Oxygen concentrations up to 75% are being used, precision of data at various concentrations is being increased and the study is being extended to more complex and higher molecular weight alkanes. Work on structural dependence of major yields and further research on the existence of methyne will continue.

An experiment is under way which involves the production of thermal carbon atoms by a nuclear reaction. The necessary equipment has been designed and is being currently manufactured. It involves a flow system in which high purity nitrogen, (less than 2 ppm of O_2) diluted with argon of comparable purity, is allowed to flow past the 60-inch cyclotron proton beam (run at maximum intensity). This gaseous mixture in which the carbon atoms thermalize without reacting either with the N_2 or with themselves because of dilution is then carried into a shielded reaction chember into which a slow stream of pure ethane is injected. It is hoped that this will shed light on the reactions of thermal carbon atoms.

The high yield of propanol-C^{14} from recoil reactions in the NH_3-CH_3OH system led to the prediction that propanol-C^{14} could be produced in good yield by nuclear reactor irradiation of solutions of ethylene in CH_3OH for periods of the order of one day. The first experiment confirmed these predictions and symmetrically labelled propanol-2,3-C^{14} was produced in 40% yield based on ethylene. Similar experiments with methanol-propene-1-C^{14} mixtures gave 70-80% chemical yields of specifically labelled isobutanol. The absence of n-butyl suggests a fast addition of a radiolytic hydrogen atom to propene, followed by radical recombination with the hydroxymethylene radical, as the mechanism. These radiolytic syntheses are simple and convenient methods for the preparation of the labelled compounds. Work on radiation synthesis, which has been so successful in producing specifically labelled alcohols, will be continued and expanded.

In the next year it is planned to study further the isotopic effect in hot atom chemistry. An almost ideal candidate is the metal-organic

HOT ATOM CHEMISTRY

(continued)

crystal ruthenocene ($Ru(C_5H_5)_2$): here the yields of the parent compound can be evaluated for three separate isotopes, Ru-97, 103, and 105, following neutron exposure. Annealing reactions will be followed, and the three isotopes compared. Additional studies of the "intrinsic" annealing range in other crystals, preferable inorganic in nature, are planned. The most likely candidates appear to be potassium chromate and bromate.

Publications

1. Harbottle, "Hot-atom Chemistry of the Solid State; its History, Current Status and Future Prospects". *Chemical Research and Chemical Techniques Based on Research Reactors* (Technical Reports Series, No. 17) IAEA, Vienna 1963, pp 149-168.

2. Apers and Harbottle, "The Szilard-Chalmers Reaction in Potassium Permanganate", Radiochim. Acta **1**, 188-93 (1963).

3. Harbottle, "The Interpretation of Annealing Reactions of Recoil Atoms in the Solid State", Proc. 1st Inter-American Conf. on Radiochemistry, Montevidea, Uruguay, July 1963.

4. Reitzner and Harbottle, "Hot-Atom Chemistry and Thermal Decomposition of Sodium Azide Crystals Containing Nitrogen-13 Recoil Atoms", Radiochim. Acta **2**, 132-38 (1964).

5. Stocklin, Stangl, Christman, Cumming, and Wolf, "The Reactions of Energetic Carbon Atoms in Methane; Oxygen and Phase Dependence; Radiation Damage Effects", J. Phys. Chem. **67**, 1735-37 (1963).

6. Wolf, "The Reactions of Energetic Tritium Atoms and Energetic Carbon Atoms with Organic Compounds", *Advances in Physical Organic Chemistry*, V. Gold, Editor, pp. 201-277, Academic Press, London, 1964.

7. Gensler and McLeod, "Fate of the Carbinol Carbon in the Conversion of Tetrahydrofurfuryl Alcohol to Dihydropyran", J. Org. Chem. **28**, 3194-97 (1963).

8. Wynberg and Wolf, "The Rearrangement of Diphenyl", J. Am. Chem. Soc. **85**, 3308 (1963).

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

J. Bigeleisen/S. Seltzer/R. E. Weston, Jr./M. Wolfsberg 5/1/64

ISOTOPE EFFECTS

It is our purpose to obtain through both experimental and theoretical investigations a basic understanding of isotope effects in physical and chemical processes. Fundamental understanding of isotope effects is important to the broadening of our knowledge in pure science. In general, isotope effects arise principally from the role of kinetic energy on energy quantization. Isotope effects are then a powerful tool for the study of quantum effects in matter; the latter are the basic principles which describe the behavior of atoms and molecules. The investigations encompass rate and equilibrium phenomena in gaseous and condensed phases. Isotope effects are an established important tool in such diverse fields as reaction mechanism investigations, geochemistry, biochemistry and molecular biology. Very important practical applications exist in the field of isotope separations. New fundamental investigations on isotope separation are undertaken when the proper occasion arises either through new scientific and technical developments or through programmatic requirements.

Much of the basic theory of the equilibrium behavior of isotopes in ideal gases has been established by rigorous statistical mechanical methods. Recent extensions of the theory to the condensed phase have resulted in the prediction and experimental discovery of new types of dynamical quantum effects in condensed matter. These results were brought to fruition by maintaining a balance of effort and strong interaction between experimental and theoretical investigations. In a similar manner isotope effects are being used to determine through experimental and theoretical investigations the basic laws governing the rates of chemical reactions and the energy surfaces involved. These investigations naturally lead to the general question of the classical and quantum mechanical description of rate processes. Isotope effects are used in the study of reaction mechanisms.

The installation of a large digital computer at BNL has already had great impact on theoretical investigations in this area. The Schachtschneider programs for the solution of problems in molecular vibration by matrix methods have been incorporated into the isotope effect programs. These programs are being made available to the scientific community. The use of large digital computers can be expected to play an important role in future theoretical and experimental research programs.

The digital computer programs will be used to further extend theoretical calculations of isotope effects. Indications have been obtained that the isotope effects for very large molecular systems can be studied

ISOTOPE EFFECTS

(continued)

theoretically by working with smaller model molecules ("cut-off procedure"). The "cut-off procedure" will be investigated in some detail. More emphasis will be given now to the analysis of experimentally observed effects and we will try to see what can be said about the force constants in transition states of specific reactions. More study is planned also of non isotopic mass effects in organic chemistry, i.e. the effect of replacement of a methyl group by an ethyl group.

We proposed previously that the restriction of the rotational and translational motion of molecules in the condensed phase will lead to interactions between these motions and the internal vibrational motions and that these interactions will lead to vapor pressure isotope effects. The theory of these interactions has been further explored and application has been made in the case of the liquid isotopic ethylenes. Further exploration of the interaction between rotational, translational, and internal vibrational motions of molecules in the condensed phase is planned. In particular one is interested in the prediction of isotope effects in the spectra corresponding to the translational and the rotational motions. Vapor pressure measurements of isotopic compounds of various symmetries will be undertaken as further tests and examples of the rotation-vibration coupling discovered in ethylene. We plan to initiate a systematic simultaneous investigation of infra-red and Raman spectra of the same molecules.

A correlation of the molal volumes of the isotopic liquid hydrogens with their zero-point energies was carried out through the use of a Grüneisen-type equation of state. Within the assumption of an isotope independent compressibility, the value of the Grüneisen constant derived from isotopic molal volumes is in reasonable agreement with that from thermal measurements and the equation of state of liquid D_2. The theoretical investigations of the zero point energies of polyatomic molecules will be studied further with the aid of a digital computer. These are of interest from the point of view of force fields in molecules, molecular vibration theory, and the structure of isotope effects.

Kinetic investigations will include the study of base catalyzed elimination reactions with a view toward the possibility of tunnelling in such reactions.

Kinetic isotope effects in some reactions of hydrogen abstraction by trifluoromethyl radicals (CF_3) will be studied. A convenient source of these radicals is the photolysis of hexafluoroacetone, and the isotope effects can be measured by isotopic analysis of the fluoromethane formed. It will be particularly interesting to examine the reactions with different isotopic species of molecular hydrogen, and to compare these reactions with the analogous reactions involving halogen atoms. In particular, it will be possible to study the "intramolecular" isotope effect in the reactions

$$CF_3 + HD \rightarrow CF_3H + D$$

$$CF_3 + HD \rightarrow CF_3D + H \quad .$$

ISOTOPE EFFECTS

(continued)

It is hoped that this system may provide a method of studying isotope effects in reactions of "hot" radicals (i.e., radicals with a kinetic energy greater than that of the surrounding medium). So far, such isotope effects have been studied only with extremely energetic atoms produced in nuclear recoil reactions.

Isotope effect studies have been continued in the decomposition of dialkyl azo compounds. A new azo compound together with its deuterated isomers was synthesized. In previous work, the magnitude of the secondary α-deuterium isotope effect indicated that azo-bis-α-phenylethane(I) decomposed thermally with both C-N bonds rupturing in a concerted manner. Additional examples of secondary isotope effects in the decomposition of dialkyl azo compounds will be studied. The role of bonding of the substituents on the azo group in determining one or two step processes will be investigated.

π-complexes have been invoked as intermediates in mechanisms of reaction as opposed to σ-complexes (or σ-bonds). When a σ-bond is formed there appears to be an inverse secondary α-effect of 10-15%. We expect to measure the effect of simple deuterated olefins (e.g., cyclohexene-1-d) in π-complex formation with Ag^+ and H_3O^+ to see if these are markedly different from those observed with σ-bond formation.

We plan to study barriers to rotation by n.m.r. The first studies will deal with cyclic amidines. These barriers will provide information about the degree of p-orbital overlap at the C-N bond and will be compared to known barriers of amides.

In the past, both in kinetic isotope effect studies and in theoretical mass spectra studies in this laboratory, the transition state formulation of rate processes has been employed. A program is now being undertaken of studying rate processes within the framework of classical mechanics by integration of the Hamiltonian equations of motion. These studies are possible because of the availability of the IBM 7094 computer. They should throw much light on the nature of reactions.

Publications

1. Seltzer, "The mechanism of a Diels-Alder Reaction," J. Am. Chem. Soc. 85, 1360-61 (1963).

2. Bigeleisen and Kerr, "Vapor-liquid Equilibria of Dilute Solutions of HT in e-H_2 and DT in e-D_2 from the Triple Points to the Critical Temperatures of the Solutions," J. Chem. Phys. 39, 763-68 (1963).

3. Bigeleisen, "Quantum Effects in Liquid," J. Chem. Phys. 39, 769-77 (1963).

ISOTOPE EFFECTS

(Continued)

4. Gold, "The Fractionation of Hydrogen Isotopes Between Hydrogen Ions and Water," Proc. Chem. Soc. 141-43 (1963).

5. Stern, Van Hook, and Wolfsberg, "Isotope Effects on Internal Frequencies in the condensed phase resulting from Interactions with Hindered Translations and Rotations - the Vapor Pressures of the Isotopic Ethylenes," J. Chem. Phys. 39, 3179-96 (1963).

6. Bigeleisen, "Molal Volumes and Zero Point Energies of the Isotopic Liquid Hydrogens," J. Chem. Phys. 39, 1356-57 (1963).

7. Stern and Wolfsberg, "Theoretical Considerations on Carbon Isotope Effects in the Decarboxylation of Malonic Acid," J. Chem. Phys. 39, 2776-77 (1963).

8. Zavitsas and Seltzer, "The Transition State in Methyl Radical Formation; the α-deuterium Effect," J. Am. Chem. Soc. 86, 1265-67 (1964).

3A8

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

R. W. Dodson/N. Sutin 5/1/64

PHYSICAL CHEMISTRY-INORGANIC REACTIONS IN SOLUTION

This work includes reaction kinetics studies, with emphasis on oxidation-reduction reactions, and studies of chemical equilibria, with emphasis on complex ion and solvent extraction equilibria.

At Brookhaven and elsewhere the problem of determining the rate of electron exchange between different oxidation states has been experimentally solved for a large number of systems by means of appropriate isotopic tracer methods. The results of research in this field have led to the development of new theories of oxidation-reduction reactions, have stimulated interest in the kinetics of redox reactions leading to net chemical change, and have given emphasis to the importance of characterizing the species present in solution, and of determining quantitatively the equilibria among them and the rates at which these equilibria are attained.

The investigation of electron exchange processes is a continuing enterprise. In close association, a program of study of the kinetics of other oxidation-reduction reactions is carried out. The development of various techniques for measuring the rates of fast reactions has opened large areas for investigation. The development of theories which predict relationships between electron exchange rates and other electron transfer processes make it particularly profitable to investigate and compare the kinetics of both types of reactions (as, for example, the exchange between Fe(II) and Fe(III) and the oxidation of Cr(II) by Fe(III)). The general aims of this work are to establish the rate laws for the reactions, to infer reaction mechanisms, to make comparisons and tests suggested by theory, and to extend the theoretical understanding of oxidation-reduction processes.

Quantitative formulation of rate laws requires a knowledge of the concentrations of the various reacting species. It is known that the same metal ion may exhibit very different redox behavior when it is in different states of coordination (e.g. Tl^{3+}_{aq}, $TlCl^{2+}$, $TlCl_2^{+}$, etc.). Hence, equilibrium studies are undertaken in connection with the kinetics program when adequate data are not available in the literature. Complex ion equilibria of interest for other reasons are also investigated.

The main techniques employed for rate measurements in this work are isotopic tracer methods, fast flow-spectrophotometric methods, and the temperature jump relaxation method. Spectrophotometric and solvent extraction methods are being used for equilibrium measurements. A collateral reason for studying solvent extraction is the wide use of this technique in chemical separations.

A result of considerable interest was obtained in experiments on the oxidation of iron(II) by cobalt(III) in the presence of chloride. The question involved was whether the electron transfer proceeds by an inner- or outer-sphere mechanism. Definite experimental evidence for inner-sphere mechanisms has hitherto been obtained only in those cases in which the transfer of a bridging group in the activated complex results in a substitution-inert species. By fast-flow methods it has now been demonstrated that the substitution labile species $FeCl^{+2}$ is the direct product of the oxidation of Fe^{2+} by $CoCl^{2+}$, and that this reaction proceeds via an inner-sphere activated complex in which the chloride is bonded directly to both the cobalt and the iron. The reactions of cobalt(III) with chloride will be measured over a wider range of temperature, hydrogen ion concentration, and ionic strength. Another system which will be studied intensively is the iron(II)-iron(III)-chloride system. It is believed that a combination of flow-spectrophotometric and isotope exchange measurements will make possible a definitive choice between electron transfer and atom transfer mechanisms for the Fe^{2+}-$FeCl^{2+}$ exchange reaction and thus answer a question of long standing in the field.

A considerable body of data on the effects of chloride on the thallous-thallic exchange reaction has been obtained in the past but could not be quantitatively interpreted because of the lack of definitive values of the stability constants of the chloro complexes of trivalent thallium. A similar problem arose in connection with recent studies of the oxidation of Cr(II) by Tl(III) in the presence of chloride. Solvent partition equilibria of thallium chlorides have been under investigation with the hope that reliable values of the stability constants of $TlCl_{3(aq)}$ and $TlCl^-_{4(aq)}$ could be obtained by this method.

It is hoped that final values of the stability constants of $TlCl_3$ and $TlCl_4^-$ and of the heats of the stepwise formation reactions will be obtained from solvent extraction measurements, and that it will be possible to relate these (satisfactorily) to results obtained by other methods. Research on the hydrolysis constants of the lower chloride complexes of thallium(III) will be extended. It is intended to use these equilibrium data to obtain more accurate formulations of the rate laws for redox reactions involving trivalent thallium. It is hoped that the available data for the extraction of thallic chlorides by diisopropyl ether can be interpreted, and that the problem of varying aggregation in the ether phase can be clarified.

A study of the extraction of methylene blue perchlorate presently under way will be extended to lower concentrations (less than 1×10^{-6} M), if possible, in order to measure a distribution coefficient for the ionized salt as well as an ion pair formation constant in the organic phase. The

PHYSICAL CHEMISTRY-INORGANIC REACTIONS IN SOLUTION

(Continued)

state of aggregation of $Hg(SCN)_2$ in water will be further studied, and an attempt will be made to disentangle the $HgCl_2$-$Hg(SCN)_2$ equilibria. Extractions with isoamyl alcohol and with trioctylphosphine oxide in hexane are promising for this purpose. A comparison of conductance and extraction coefficient methods for estimating ion-pair formation constants in non-aqueous solvents will be undertaken.

Publications

1. Dulz and Sutin, "The Kinetics of the oxidation of Iron(II) and its Substituted tris-(1,10-phenanthroline) Complexes by Cerium(IV)," Inorganic Chem. 2, 917-21 (1963).

2. Diebler and Sutin, "The Kinetics of Some Oxidation-Reduction Reactions Involving Manganese(III)," J. Phys. Chem. 68, 174-80 (1964).

3. Campion, Purdie, and Sutin, "The Rate of the tris-(2,2'-dipyridine)-Osmium(II)-Octacyanomolybdate(V) Electron Transfer Reaction," J. Am. Chem. Soc. 85, 3528 (1963).

4. Dulz and Sutin, "The Effect of Chloride Ions on the Kinetics of the Oxidation of Chromium(II) by Iron(III)," J. Am. Chem. Soc. 86, 829-32 (1964).

5. Craig and Sutin, "The Mössbauer Effect in Liquids: Influence of Diffusion Broadening," Phys. Rev. Letters 11, 460-62 (1963).

6. Nancollas and Sutin, "The Kinetics of Formation of the Nickel Monooxalate Complex in Solution," Inorganic Chem. 3, 360-64 (1964).

7. Conocchioli, Nancollas and Sutin, "The Oxidation of Iron(II) by Cobalt(III) in the Presence of Chloride Ions," J. Am. Chem. Soc. 86, 1453-54 (1964).

8. Marcus, "Interactions in Polar Media. II. Continua," J. Chem. Phys. 39, 460-469 (1963).

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

S. Ehrenson 5/1/64

PHYSICAL CHEMISTRY-THEORETICAL ORGANIC CHEMISTRY

These researches are concerned with the structures and reactivities of organic systems. The methods of attack include linear free energy relationship of the Hammett-Taft type as well as semi-empirical quantum mechanical calculations by the LCAO-MO method. Attempts are made to interrelate the two approaches with the hope of providing quantum mechanical bases for the linear free energy relations.

Substituent effects in aromatic and aliphatic systems are being investigated with improved Hückel and Pariser-Parr wave functions. The electrostatic approaches of Kirkwood-Westheimer and Branch and Calvin are employed within the framework of the Taft equation. A priori statistical reevaluation of the parameters from experimental data is proceeding by means of fast computers. These parameters provide the bases for the linear free energy comparisons and, if these are to be significant, they must be established reliably.

Empirical refitting of the Taft parameters has been carried out with special emphasis on the σ^o reactivities. These apply to reactions in which resonance is precluded between the substituent and reaction center. These reactions provide a good basis from which to construct a set of linear free energy parameters. In particular, it has been found that meta inductive effects are, in fact, proportional <u>but</u> <u>not</u> <u>equal</u> to the para effects. These have formerly been explicitly assumed to be equal to one another. The implications of this result to tne problem of separation of resonance and inductive effects is under investigation. The statistical fitting of linear free energy parameters will be continued with emphasis on benzoic type reactivities and extensions to nucleophilic and electrophilic reactions. Further studies of the relationship of aromatic to olefinic reactivities will be carried out.

The hydrolysis of olefins and dehydration of alcohols have been selected as prototype reactions involving carbonium ions. Electronic energies have been calculated by the Wheland-Mulliken MO method with self-consistent charge redistribution. Hyperconjugation gives significant stabilization to carbonium ions derived from alkyl substituted olefins by proton addition. These results show that hyperconjugation alone suffices to explain the Baker-Nathan effect, and the Markownikoff and Saytzeff-Wagner addition rules. Contrary to experimental indication, these theoretical calculations predict relative C-H to C-C hyperconjugative effects to be the same in olefinic and aromatic systems undergoing similar reactions.

Additional experimental studies of the role of hyperconjugative stabilization of carbonium ions are intended. Evidence for hindered rotation in protonated alkyl anthracenes will be sought.

PHYSICAL CHEMISTRY-THEORETICAL ORGANIC CHEMISTRY

(Continued)

The structure of Yang's molecule, tris di-t-butyl p-phenoxy methyl radical, will be investigated by X-ray diffraction with the hope of determining whether the ground state is a triplet or biradical. Unpaired spins have been demonstrated by magnetic measurements.

Publications

1. Ehrenson, "A Priori Refitting of the Taft Equation by Non-linear Least Squares Methods," Tetrahedron Letters #7, 351-7 (1964).

2. Ehrenson, "Hyperconjugation Theory of Carbonium Ion Reactions," J. Am. Chem. Soc. 86, 847-54 (1964).

3A10

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

L. Friedman/J. C. Chen 5/1/64

PHYSICAL CHEMISTRY--MOLECULAR EXCITATION AND REACTIONS IN THE GAS PHASE

This work is concerned with the interactions of electrons and of positive ions with molecules in the gas phase. Such interactions must be directly involved in the radiation chemistry of gases. They also bear on a fundamental problem in chemical kinetics, namely the way in which the kinetic energy of colliding reactants is converted into internal energy, of vibration or rotation, and thus becomes available for chemical reaction.

A considerable body of experimental data on the excitation of molecular vibrations by electron impact has been obtained in other laboratories. At Brookhaven theoretical studies of the phenomena have been undertaken. There is good prospect of success in formulating a theoretical treatment for these effects.

Research on ion-molecule reactions is readily carried out with mass spectrometers, and comprises one of the applications of our mass spectrometric facilities to basic research in chemistry. The unique aspect of ion-molecule reactions is that is is possible to control the kinetic energy of the reactant ions by the simple application of an electric field. In general this does not alter the internal energy of the ion. With hydrogen molecule ions it is possible to compute the internal energy states produced in the electron impact process used to generate these ions. In this way reactions can be studied with species of known internal energy as well as controlled kinetic energy, and significant results on the energy transfer process can be derived. For example, it has been shown that the flow of kinetic energy to internal energy in such processes as the reaction of

$$H_2^+ + He \text{ --- } HeH^+ + H$$

is a relatively improbable process and that the energy required to produce the proper configuration in H_2^+ for reaction must be present prior to collision of the reactants. The object of this research is to study a variety of ion-molecule systems to obtain more detailed information on the nature of energy transfer processes in reactive collisions.

Theoretical calculations have been continued on excitation and de-excitation of molecular vibration by slow electron impact. A mechanism has been proposed which involves compound negative ion

PHYSICAL CHEMISTRY--MOLECULAR EXCITATION AND REACTIONS IN THE GAS PHASE (continued)

states as intermediates. Numerical calculations have been carried out for the nitrogen molecule. The multi-peak structure observed in experimental excitation functions has been accounted for. Calculations of the total cross section for vibrational excitation of ground state N_2 are in good agreement with experiment.

The theoretical methods developed for electron-molecule interactions will be extended and tested further by comparison with experiment. Energy transfer in ion-molecule reactions will be studied in the systems $HD-N_2$, $HD-O_2$, $HD-CO$, $HD-N_2O$, and $HD-CO_2$. These combinations are selected because of the availability of supplementary information on the properties of N_2^+, O_2^+, CO^+, N_2O^+, CO_2^+, etc. The general objective is to find systems which are relatively simple and still of chemical interest, and which will provide sufficient information for critical tests of theoretical models of the processes.

Publications

1. Chen, "Unitary Operator Formalism of the Eigenvalue Problems", J. Chem. Phys. 39, 3167-70 (1963).

2. Chen, "Anharmonicity Effects in Vibrational Excitation of Molecules by Slow Electron Impact", Physics Letters 8, 183-4 (1964).

3. Chen, "Off-diagonal Hypervirial Theorems and Their Applications", J. Chem. Phys. 40, 615-21 (1964).

4. Moran and Friedman, "Neon-hydrogen Ion Molecule Reactions", J. Chem. Phys. 39, 2491-2500 (1963).

5. Moran and Friedman, "Application of the Platt Electrostatic Model to Diatomic Hydride Ions", J. Chem. Phys. 40, 860-66 (1964).

3A11

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

S. Freed 5/1/64

PHYSICAL CHEMISTRY--BIOCHEMICAL PROCESSES

Two lines of research on biochemical problems are being pursued. In one, techniques developed here for studying reactions in solution at low temperatures are applied to enzyme reactions. In the other, radioactive tracers are employed to facilitate the detection of possible chemical changes connected with learning by planarians.

Enzyme reactions are being studied in suitable liquid solvents at temperatures between 0°C and -80°C. The aim is to retard reactions which are rapid at room temperature in order to observe reversible intermediate reactions, even when the room temperature reactions are irreversible. It is also hoped that the isolation of intermediate substances and direct study of their properties will prove to be possible. The results should contribute some clarification to the understanding of normal biochemical processes, and may also help provide a chemical basis for studies of viability and long-term preservation of biological systems at low temperatures.

It has been shown by others and confirmed here that planarians, the lowest species in the evolutionary scale possessing a central nervous system, can learn by conditioned reflex and by running mazes. After transection across the length of a trained planarian and subsequent regeneration into two complete worms, each requires considerably fewer trials than the untrained planarian to reach the criterion of learning. In experiments at the University of Rochester it was shown that if the subsequent regeneration took place in a bath containing the enzyme ribonuclease, the worm regenerated from the head portion exhibited the same reduction in the number of trials required for criterion of learning as when regenerated in pond water; but the worm regenerated from the tail portion had lost its stored information, i. e., it now required about the same number of trials as an ordinary, untrained planarian. Ribonuclease hydrolyzes ribonucleic acid into its component mononucleotides, and thus disintegrates the ordering with the information contained in these macromolecules. This experiment indicated that the macronucleic acids were implicated in the learning process and in the transmission of the information from the ganglia in the head to the tail of the planarians.

The studies in progress are directed to the chemical characterization of changes in the macromolecules of planarians synthesized by them during learning.

Techniques and systems of solvents have been developed for carrying out enzymatic reactions below 0°C. α-chymotrypsin has been studied in some detail and exploratory work has been done with a few dehydrogenases.

An intermediate reaction of lactic acid dehydrogenase, its union with the co-enzyme DPNH, was found to occur with great rapidity at -80°C.

Whereas aqueous solvents containing 42% or more methanol denatured α-chymotrypsin rapidly at room temperature, at -33° an 80% methanolic solution permitted the catalytic hydrolysis of its specific substrate acetyl tryptophane ethyl ester.

A systematic study was made of the influence of methanol concentration and temperature on the activity of α-chymotrypsin from 25° to -33°C.

Between 15° and -33°C much of the enzymatic behavior proceeded regularly. The measurements at the lowest temperature were made possible by a new fluorometric assay of α-chymotrypsin.

Indications have been obtained, using P-32 tracer, of a difference in the amounts of the nucleic acids laid down in planarians during the learning processes(in conditioning) as compared with planarians that were given the same number of stimuli but randomly applied.

In addition to further studies of enzymes, chemistry of nucleic acids will be explored at low temperatures.

The experiments on nucleic acid formation in planarians during learning will be repeated with finer chemical discriminations and with better controls. Analyses of the ratios of the different mononucleotides within the nucleic acids will also be made.

Work is also being started on the chemistry of the nervous systems of horse-shoe crabs, to compare changes in the nucleic acids associated with learning. This program, as well as the one with planarians, is being carried out with the participation of a member of the staff of Michigan State University.

Publication

1. Bielski and Freed, "Fluorimetric Assay of α-Chymotrypsin", Anal. Biochemistry 7, 192-98 (1964).

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

L. M. Corliss/N. Elliott/W. C. Hamilton 5/1/64
J. M. Hastings/J. A. Ibers/E. V. Sayre

MOLECULAR AND CRYSTAL STRUCTURE

Neutron diffraction is being extensively used to investigate fundamental characteristics of magnetic materials. The interaction of neutrons with an ordered array of atomic magnetic moments gives rise to scattering and a characteristic diffraction pattern quite analogous to the patterns obtained when x-rays are scattered from solids. The magnetic pattern is superimposed on the diffraction pattern which arises from the nuclear scattering and can be separated from it by appropriate techniques. In ferromagnetic and antiferromagnetic materials, the repeat pattern of atomic magnetic moments can be obtained, as well as the magnitude and orientation of individual moments. This knowledge of the magnetic structure is fundamental to the understanding of magnetic properties; it provides a framework for theoretical calculations and an essential check on the validity of concepts of the origin of magnetism. The Chemistry Department program has emphasized the study of the relationship between magnetic structure and crystal structure, with the long-range objective of elucidating the nature and mechanism of interatomic magnetic interactions in solids. Interest has also been focused on the magnetic ordering process, magnetic transitions, and the spatial distribution of magnetic electrons. In FY 1965 the High Flux Beam Reactor at BNL will become available for experimental research. This unique facility will place significantly more intense neutron beams at our disposal, making it possible to increase resolution, sensitivity, and data-collection speed. The scope of the experimental program will be extended to areas of research which are inaccessible at the present reactor. These include neutron spectroscopy and inelastic scattering, by means of which the dynamical properties of magnetic as well as non-magnetic crystals can be studied.

Crystallography continues to constitute the best method for the precise and unambiguous determination of molecular structure. In combination with other physical measurements, it provides the key to the understanding of chemical bonding and hence of reactivity, mechanisms, the interpretation of spectra, etc. The unique combination of x-ray diffraction, neutron diffraction, and outstanding computational facilities at Brookhaven has made possible a broad and comprehensive attack on significant problems in organic, inorganic, and physical chemistry. The neutron diffraction installations have been invaluable in the determination of the structure of hydrogen-containing compounds and in the study of hydrogen bonding in the solid state. The use of digital computers has in the past few years revolutionized crystallography, and we continue to devote considerable effort, not only to the routine computations of crystallography, but to the use of the extraordinary speed and capacity of the modern digital computer to develop methods of automatic solution of crystal structures directly from intensity data.

The development of the modern x-ray diffractometer, using a scintillation counter, and the resulting improved accuracy, have made it possible in principle to determine atomic charge by measuring reflection intensities at low scattering angles. Research in this field is being carried out on a number of simple compounds with known structures for which favorable x-ray reflections occur.

The incorporation of ions and molecules within crystals affects the optical properties of these entities. Spectral changes that intrinsically reflect the periodicity of the lattice (space group effects) as opposed to those that arise solely from the local crystal field acting on the chemical unit (point group effects) have been heretofore investigated only in organic molecular crystals. These investigations have been very limited in scope and the results have not been fully understood. Examples of such interactions in inorganic ionic crystals are being sought and investigated with the expectation that improved understanding of these complex effects will result.

During the coming year a substantial fraction of the experimental equipment including the powder diffractometer, three-crystal inelastic scattering spectrometer and two single crystal units will be installed at the HFBR. It is expected that the powder unit will be available for use during the startup program of the reactor. In addition, the single-computer control of all the jointly operated Chemistry and Physics spectrometers should become operative in FY 1965. The on-line computer control system, designed in collaboration with the Applied Mathematics and Instrumentation Departments, should provide a very flexible and powerful method of data acquisition and processing which will enhance the usefulness of the spectrometers.

The study of intermetallic systems containing rare earth metals now underway will be continued. Interest in these compounds stems from the unusual magnetic structures previously observed with neutrons as well as from the anomalous moments inferred from magnetic measurements and attributed by some to very large crystal field effects. The precise direction of this effort will depend on the outcome of neutron diffraction investigations currently in progress ($ErMn_2$, $TmMn_2$, $TbNi_2$, $HoGa_2$).

MOLECULAR AND CRYSTAL STRUCTURE

(continued)

Work on magnetic oxides, directed largely by an interest in superexchange mechanisms, is expected to continue along lines closely related to our activities in the past; interesting possibilities are being explored at the present time. The study of the magnetic scattering from single crystals of Cr_2O_3, already under way, will be pursued with both polarized and unpolarized neutrons in order to determine whether canting of the basic antiferromagnetic spin system occurs. This point appears to be essential to a complete understanding of magnetic and magnetoelectric phenomena. Observation should be resolvable through a proper understanding of space group interactions.

It is expected that the present infrared and Raman research will lead to similar studies in the field of electronic and vibronic spectra.

Publications

1. Ibers and Smith, "Crystal Structure of a Sodium Cobalt Molybdate", Acta Cryst. 17, 190-97 (1964).

2. Hamilton and Ibers, "Structures of $HCrO_2$ and $DCrO_2$", Acta. Cryst. 16, 1209-12 (1963).

3. Hamilton and Ibers, "X-ray Investigation of the Crystal Structures of Xenon Tetrafluoride", Noble Gas Compounds, H. H. Hyman, Editor, pp. 195-202, University of Chicago Press, 1963.

4. Manoharan and Hamilton, "The Crystal Structure of Sodium Nitroprusside", Inorganic Chem. 2, 1043-47 (1963).

5. Hamilton, Ibers, and Mackenzie, "The Geometry of the Perxenate Ion", Science 141, 532-34 (1963).

6. McGaw and Ibers, "The Nature of the Hydrogen Bond in Sodium Acid Fluoride", J. Chem. Phys. 39, 2677-84 (1963).

7. Ibers, "Refinement of Patterson and Levy's Neutron Diffraction Data on KHF_2", J. Chem. Phys. 40, 402-4 (1964).

8. LaPlace and Ibers, "Studies of the Metal-Hydrogen Bond: Structure of $HRh(CO)(P(C_6H_5)_3)_3$", J. Am. Chem. Soc. 85, 3501-2 (1963).

9. Eisenberg, Ibers, Clark and Gray, "Molecular and Electronic Structure of the *Bis*-(maleonitriledithiolato)-nickelate(II) Ion", J. Am. Chem. Soc. 86, 113-15 (1964).

3A13

BROOKHAVEN NATIONAL LABORATORY Chemistry Department

R. W. Stoenner/D. Christman/L. Friedman
E. V. Sayre/M. Slavin

5/1/64

ANALYTICAL CHEMISTRY

Chemical and spectrographic analyses are performed in support of the Laboratory's research program. This is a continuing service activity geared to the requirements of current research. About three-fourths of the activity is required in support of research in the Chemistry Department, while the remainder is in support of work in other departments, principally Nuclear Engineering. Some research on analytical methods related to topics of immediate interest is carried out.

Analytical mass spectrometry services have been provided in the Chemistry Department, in the form of gas analyses, isotopic ratio analyses, and the analysis of solid materials. This work has supported a variety of research programs in Chemistry, and in the Biology, Reactor and Accelerator Departments of BNL. Laboratory facilities include: a 180°-5" radius single collector gas analysis spectrometer, two precision isotope ratio mass spectrometers and a double focussing spark source mass spectrometer. One isotope ratio mass spectrometer serves for precision analysis of hydrogen isotopes, the other is used for C^{13}, N^{15} and O^{18} assays.

Service analyses in support of organic chemical research is provided. Included in this activity are conventional carbon, nitrogen, halogen and sulfur assays, and carbon-14, tritium and deuterium assays.

Neutron activation analysis is finding application in a number of areas of research. Advantage is taken of the non-destructive aspect of this method of analysis in the examination of paintings and of ancient artifacts. The extreme sensitivity of activation analysis is utilized in the analysis of meteorites and mineral separates from meteorites.

Chemical analysis is being applied to archaeological artifacts to determine the nature and sources of raw materials used in their manufacture and also the technological methods employed in antiquity. In some instances compositions are so characteristic of particular regions and periods that they can be employed as evidence for authentication and dating.

The possibility of establishing autoradiography of oil paintings following neutron activation as a nondestructive method of revealing detailed information of the structure, condition and distribution of pigments within the paintings is being explored.

Considerable effort has been expended to develop the double focussing spark source mass spectrometer into an instrument with high sensitivity, sufficient to permit analysis of nuclear reaction products. The object of such studies is to gain more complete mass yield curves on products of nuclear reactions, that is, to measure yields of stable long-lived nuclides which resist detection or measurement by ordinary counting techniques. Samples of fission products in U^{235} matrices have been analyzed with the object of accurately determining sensitivity and relative ionization and collection efficiencies of the trace constituents. Partial mass yield curves from U^{235} fission were obtained from samples which contained 15 ppm of the more abundant fission products. These studies showed that analysis of products of nuclear reactions in targets irradiated in the BNL high energy accelerator will require chemical as well as instrumental techniques. Studies are now under way on methods which include one stage of chemical separation of nuclear reaction products from the major constituents of the target matrix. So far, sensitivity which permits detection of 10^{-10} grams of rare earth nuclide has been achieved. This sensitivity is adequate for nuclear reaction studies provided that problems of background contamination of target and reagent materials can be solved. There problems are currently under investigation.

It is hoped that the studies of ancient glass and archeological objects will be completed during the next year. The thermal neutron activation examination of paintings will be directed toward a more quantitative estimate of the damage hazard involved, and to evaluate more fully the range of applicability.

Potassium assays for purposes of age determination by the potassium-argon method are being completed on a series of five mineral separates from the Indarch meteorite.

The development of a spectroscopic method for the direct determination of deuterium in water by closed tube electrodeless discharge is continuing.

Publication

1. Sayre, "Methods and Applications of Activation Analysis", Ann. Rev. Nucl. Sci. 13, 145-62 (1963).

SECTION 3B

BROOKHAVEN NATIONAL LABORATORY - NUCLEAR ENGINEERING DEPARTMENT

3B1	Physical Chemistry of High Temperature Systems
3B2	Mechanism of Pyrolytic-Graphite Formation
3B3	Radiation Chemistry of Fluorocarbon and Noble Gas Chemistry
3B4	Fluoride Volatility Studies Related to Reprocessing of Reactor Fuels
3B5	Solvent Extraction of Polyiodides and Hydration Numbers of Extracted Salts
3B6	Mechanism of Fission Fragment Induced Reactions
3B7	Mechanism of Radiation Induced Reactions in Organic Materials
3B8	Chemistry of Actinides
3B9	Electrochemical Studies in Fused Salts
3B10	Preparation and Purification of Special Isotopes for Research

For further information on work completed, the reader is referred to the open scientific literature and to the Brookhaven National Laboratory Annual Report, July 1, 1964. The report number is BNL 867(AS-18) Publication is expected by November, 1964.

BROOKHAVEN NATIONAL LABORATORY
Upton, New York

Nuclear Engineering Department

J. J. Egan

1/2/64

PHYSICAL CHEMISTRY OF HIGH TEMPERATURE SYSTEMS

The purpose of this program is the development of physico-chemical techniques for studying high temperature systems of interest in nuclear technology, as well as supplying thermodynamic data on these systems. Electrochemical methods in both the liquid and solid state along with spectroscopic techniques are stressed.

Chronopotentiometry and spectrophotometry are being used to study metals dissolved in their own molten halides. Solid state electromotive force methods are employed to obtain free energies of formation of chlorides, fluorides, and carbides at high temperature. The thermodynamic properties of molten salt solutions are being systematically studied by an emf technique using only gaseous electrodes. Liquid metal mixtures whose thermodynamic properties are influenced by their electronic constitution are also being examined by the use of emf cells with solid electrolytes.

Publications

1. Egan, "The Standard Molar Free Energy of Formation of ThC_2 by Electromotive Force Measurements," J. Phys. Chem. (in press, to appear in March 1964).

2. Van Norman and Egan, "The Mg-$MgCl_2$ System - A Chronopotentiometric Study," J. Phys. Chem. 67, 2460 (1963).

3. Egan, McCoy, and Bracker, "The Standard Molar Free Energy of Formation of $MgCl_2$,$CeCl_3$,UCl_3, and $ThCl_4$ From EMF Measurements" in "Thermodynamics of Nuclear Materials," p. 163, I.A.E.A., Vienna, 1962.

4. Wiswall, R. H. and Egan, J. J., "Thermodynamics of Solutions of Actinides and Fission Products in Bismuth" in "Thermodynamics of Nuclear Materials", p. 345, I.A.E.A., Vienna, 1962.

BROOKHAVEN NATIONAL LABORATORY
Upton, New York

Nuclear Engineering Department

John Clarke

12/19/63

MECHANISM OF PYROLYTIC-GRAPHITE FORMATION

To establish the conditions under which graphite deposits rather than evaporates when in contact with a hydrocarbon-hydrogen system, it is necessary to know the sublimation temperature of graphite as a function of C/H ratio and pressure. These fundamental curves have been calculated by Duff and Bauer using speculative thermodynamic calculations and involve free radicals such as HC_x. The experimental determination of these sublimation curves is the first objective of the present program.

Experimental studies at BNL have verified the calculated sublimation temperatures in the temperature range 2100° to 2400°C at 0.1 atmospheres, and indicate that equilibrium is rapidly established at the graphite surface. The product gas contains unexpected CH_4 which probably results from subsequent gas-phase reactions. The presence of argon increases the yield of C_2H_2, but also increases the sublimation temperature. Future work will extend the range of the sublimation temperature determinations. In addition, an investigation will be made to determine how the species present condense and rearrange on a growing graphite surface.

In associated work, a rapid method* of measuring the surface area of graphites using Kr^{85}-traced Kr has recently been developed which allows one to determine the surface area of graphite of any geometric form and also determine the surface area of the internal closed pores.

*submitted to J. Phys. Chem., Nov. 1963

BROOKHAVEN NATIONAL LABORATORY
Upton, New York

Nuclear Engineering Department

D. R. MacKenzie

1/2/64

RADIATION CHEMISTRY OF FLUOROCARBON AND NOBLE GAS CHEMISTRY

Fluorocarbon research involves investigation of the effects of heat and radiation on pure fluorocarbons. The materials studied to date include the cyclic compounds F-benzene, F-biphenyl, F-naphthalene, and their saturated analogues F-cyclohexane, F-bicyclohexyl and F-decalin (where F-stands for perfluoro). All have been highly purified by preparative scale gas-liquid chromatography.

Most irradiations have been done in thin window nickel cells using 1.5 Mev electron beam from a van de Graaff accelerator. Results of irradiations at temperatures up to 100°C indicate that in this temperature range G_{gas} for the aromatic fluorocarbons is negligible, but $G_{polymer}$ is 2 to 3 times that for the corresponding hydrocarbons. The alicyclics, however, are more stable than the corresponding hydrocarbons, and have G-values for consumption of starting material similar to the aromatic fluorocarbons.

Two distinct aspects are now taking shape in the program. One concerns the effects of high temperature on radiation stability of the less volatile compounds, including F-o-terphenyl, which will be available soon. The other involves fundamental studies on the mechanism of radiolysis of one or more of the lighter compounds, using scavengers and radiations of different LET.

Compounds of fluorine with the noble gases, xenon and krypton, have been prepared at room temperature and lower using γ-rays, 1.5-Mev electrons and 10-Mev protons. Attempts to prepare other binary noble gas compounds are being made. The radiation chemistry of xenon fluorides is being studied.

Publications

1. MacKenzie and Wiswall, Jr., "Compound Formation by γ-Irradiation of Xenon-Fluorine Mixtures," Inorg. Chem. 2, 1064 (1963).

2. MacKenzie and Wiswall, Jr., "The Synthesis of Xenon Compounds in Ionizing Radiation." In "Noble-Gas Compounds," University of Chicago Press, 1963, edited by H. H. Hyman.

3. Hamilton, Ibers and MacKenzie, "Geometry of the Perxenate Ion," Science 141, 532 (1963).

3B4

BROOKHAVEN NATIONAL LABORATORY Nuclear Engineering Department

Gerald Strickland 12/26/63

FLUORIDE VOLATILITY STUDIES RELATED TO REPROCESSING OF REACTOR FUELS

Anhydrous solutions of HF containing N_2O_4 will attack reactor fuels containing U, UO_2, UC_2, Pu, Zr, Al, Be, BeO, Mo, stainless steel and graphite. Practical rates are obtainable in a 25 M % NO_2 solution at 100-150°C. Solutions containing N_2O_3, or NOF and N_2O_3, are also useful but do not attack graphite. Studies at this laboratory on the chemistry of these solvents have shown that their unusual reactivity is due to the formation of NO^+ and F^- ions. Distillation studies aided by vapor infrared analysis have revealed the existence of two or three azeotropes in these systems.

These solvents are used as dissolving agents in the Nitrofluor process which is being developed as a simplified method of treating a variety of reactor fuels. Uranium and its compounds are converted to $NOUF_6$ which is subsequently volatilized as UF_6 by treatment with BrF_3 or BrF_5. The $NOUF_6$ is also volatile under conditions not yet completely defined; whereas the Pu compound apparently is not and requires F_2 for conversion to PuF_6.

Problems related to the engineering-scale dissolution of enriched fuels will be examined using Monel and nickel equipment. These materials owe their corrosion resistance to films which are fairly protective and are under study. Uranium recovery work will follow that on dissolution.

BROOKHAVEN NATIONAL LABORATORY
Upton, New York

Nuclear Engineering Department

B. Manowitz/L. Slater

1/2/64

SOLVENT EXTRACTION OF POLYIODIDES AND HYDRATION NUMBERS OF EXTRACTED SALTS

It has been found that alkali metal cations can be extracted from aqueous solutions into organic solvents of high dielectric constants such as polyiodides. Extraction of sodium, potassium, rubidium, and cesium from sodium iodide solutions into solutions of iodine in nitrobenzene, usually at 25°C, has been studied. Extraction coefficients have been high, ranging from as much as six for sodium to two thousand for cesium. It has been shown that polyiodide anions as complex as the enneaiodide, I_9^-, are involved in extractions.

Preliminary values of the formation constants, at 25°C in nitrobenzene, of the pentaiodide, heptaiodide and enneaiodide ions have been obtained. An estimate has been made of the formation constant of the triiodide ion. Approximate values of hydration numbers of extracted sodium ion have been determined. More detailed study of the extraction of alkali polyiodides will be made. More accurate values of the formation constants and hydration numbers will be made at temperatures ranging from 10° to 40°C. From these it is hoped to obtain thermodynamic data on the various complex anions.

It has also been found that rare earth and alkaline earth cations may be extracted from aqueous iodide solutions by solutions of iodine in nitrobenzene. Even though extraction coefficients are lower than for alkali metal cations the mechanisms of extraction should be studied.

Publication

1. Slater, "Extraction of Sodium and Cesium Polyiodides into Nitrobenzene," Nuclear Sci. and Eng., 17, 576-585 (1963).

BROOKHAVEN NATIONAL LABORATORY
Upton, New York

Nuclear Engineering Department

B. Manowitz/L. Slater

1/2/64

MECHANISM OF FISSION FRAGMENT INDUCED REACTIONS

It is desired to study the mechanism of fission fragment induced reactions. However, associated with fission fragments are neutrons, gamma rays, and other radiation. It is difficult to separate the effects of fission fragments from those of less energetic radiation. Alpha particles have linear energy transfer (LET) values much closer to those of fission fragments than do other radiations. Thus, the study of alpha particle induced reactions would shed much light on the mechanism of fission fragment induced reactions.

An alpha source calibrator has been built. This consists of a solid state charged particle detector mounted in a vacuum chamber at some distance from a polonium-210 alpha source. The distance from source to detector as well as the size opening to the detector may both be varied. The alpha source may be rotated and tipped. Thus the spectrum and number of alpha particles leaving the source at all angles may be determined. This should result in better values for energy deposited in a system than obtainable from chemical dosimetry. In addition, effects due to varying initial LET values may be determined.

Simple gaseous systems will be studied. The first will be the alpha particle induced formation of ozone from oxygen at various temperatures. The effect of different impurities and of dose rate variation will be studied. After this it is hoped to study other simple reactions leading to a better understanding of the mechanisms of reactions induced by high LET particles.

BROOKHAVEN NATIONAL LABORATORY
Upton, New York

Nuclear Engineering Department

D. S. Ballantine

12/19/63

MECHANISM OF RADIATION INDUCED REACTIONS IN ORGANIC MATERIALS

Solid state polymerization of pure acrylamide and mixed with propionamide has been studied by chemical spectrsocopic techniques. Diffusion of monomer at defects and interfaces probably plays an important role. Future studies are aimed at testing quantitatively mathematical expressions for the diffusion processes.

Radiolysis studies of this system in which gaseous products are analyzed suggest that energy transfer and/or radical scavenging reactions are important. Future ESR experiments should permit some differentiation between these alternatives. Other systems will also be studied.

A second effort involves a systematic study of a series of substituted aromatic hydrocarbons under varying conditions of dose, temperature, physical state and LET. Data have been obtained for toluene and xylene and further compounds will be selected to test the effect of polar substituents on the radiation initiated reactions.

A third study involves the role of ions in liquid organic reactions. One aspect of this work will be a continuation of polymerization studies of styrene and related monomers by classical kinetic techniques to determine to what extent ions are involved in recently found abnormally high rates of reactions.

A more fundamental aspect of this study involves development of an ion detection technique based on measurement of dielectric loss as a function of frequency. Future effects will be directed toward reduction of the already successful qualitative technique to a quantitative method. Ultimately the technique should be applicable to the determination of w values for ion yields in liquid systems.

Publications

1. Baysal, Adler, Ballantine and Glines, "Polymer Fractionation Studies in the Solid State Polymerization of Acrylamide," Polymer Letters 1, 257-62 (1963)

2. Baumann, and Metz, "Gamma Radiation Induced Polymerization of Alpha-Methylstyrene. The Effect of Water on Molecular Weight Distribution," J. Polymer Sci. 62, (174), S141-S144, (1962)

BROOKHAVEN NATIONAL LABORATORY
Upton, New York

Nuclear Engineering Department

Leonard Newman/Paul Klotz/Jack Fajer

1/2/64

CHEMISTRY OF ACTINIDES

The synergistic effect of tri-n-octylamine on the solvent extraction of thorium by thenoyltrifluoroacetone (TTA) has been shown to arise from the organic phase reaction $ThT_4 + R_3NHCl \rightleftharpoons ThT_4R_3NHCl$, where R_3NHCl represents the amine hydrochloride and T^-, the enolate ion of TTA. The formation constant for this reaction was measured in benzene as 260 ± 40. A similar study on the solvent extraction of americium is underway.

An investigation of the hydrolysis of cerium has been completed and submitted for publication. EMF data indicate that at most, one percent of the Ce(III) ions can be transformed into the hydrolysis products without formation of a precipitate; this is explained by assuming the equilibrium:

$$3\ Ce^{+++} + 5\ H_2O \rightleftharpoons Ce_3(OH)_5^{++++} + 5\ H^+$$

Further hydrolysis studies on the actinides are planned.

We have investigated the reduction of piaselenols, the selenium chelates of 1,2 diaminobenzene and related ligands. Solutions of diamagnetic piaselenol undergo chemical and electrochemical reduction to form a red paramagnetic species. Chemical reductions with Na or Li were carried out in tetrahydrofuran, and electrochemical reactions in acetonitrile. ESR data show partial delocalization of the spin density. Polarography shows a half-wave potential of -1.35 v. vs. S.C.E.; coulometric reduction at -1.4 v., at a Hg pool, yields the red paramagnetic species. The original compound can be regenerated by air oxidation as shown by absorption spectra. This work will be continued.

Publications

1. Newman, and Klotz, "Synergistic Effect of Tri-n-octylamine on the Solvent Extraction of Thorium by Thenoyltrifluoroacetone," J. Phys. Chem., 67, 205 (1963).

2. Newman, "On the Synergistic Effect in Solvent Extraction," J. Inorg. Nucl. Chem., 25, 304 (1963).

BROOKHAVEN NATIONAL LABORATORY
Upton, New York

Nuclear Engineering Department

Clemens Auerbach/Stephen Feldberg/George Kissel

1/2/64

ELECTROCHEMICAL STUDIES IN FUSED SALTS

The low melting point (132°C) of $LiNO_3$-KNO_3 eutectic makes it well suited for investigations at the dropping mercury electrode (DME). It is interesting that the half-wave potentials of lead and cadmium in $LiNO_3$-KNO_3 are virtually coincident, in contrast to their 0.2 v. separation in common aqueous media at room temperature. It has been shown that this behavior is not simply a temperature effect but reflects specific solvent-solute interaction, probably preferential coordination of lead by nitrate. As a result it is planned to undertake potentiometric studies in a non-coordinating solvent of similar melting point, such as dimethylsulfone, in which the nitrate concentration can be varied.

Other polarographic work has included initial studies on the anodic dissolution of the DME in molten nitrate media containing such depolarizing anions as chloride, bromide and hydroxyl. Chronopotentiometry, especially with current reversal, is considered to be a powerful technique for studies of this type, and work along these lines will be continued.

Work is now in progress on uranium in EDTA-containing medium, a system which is of analytical interest despite certain abnormal features. The hanging mercury drop electrode, which provides a continually renewable and reproducible surface, has been found to be extremely useful in these studies.

Publications

1. Auerbach and Kissel, "Determination of Uranium at Microgram Levels by Derivative Polarography;" BNL 800 (T-307), May 1963; accepted for publication in TALANTA.

2. Feldberg and Auerbach, "A Model for Current Reversal Chronopotentiometry with Second Order Kinetic Complications;" presented at the 145th National Meeting, American Chemical Society, New York, September 1963; accepted for publication in ANALYTICAL CHEMISTRY.

3B10

BROOKHAVEN NATIONAL LABORATORY
Upton, New York

Nuclear Engineering Department

Manny Hillman

1/2/64

PREPARATION AND PURIFICATION OF SPECIAL ISOTOPES FOR RESEARCH

Reactions of Tritons: Successful use of the reactions of reactor produced tritons ($Li^6(n,t)\alpha$) for the production of F^{18} and Mg^{28} has led to a further investigation of the reaction of these tritons with other nuclides of $A < 60$. Ar^{42} from the $Ar^{40}(t,p)Ar^{52}$ and Co^{58g} from the $Fe^{56}(t,n)Co^{58}$ reactions have been observed, and a cross section of $\sim 50\ \mu b$ has been obtained for the $Ni^{58}(t,n)Cu^{60}$ reaction. Excitation functions have been obtained for the $Mg^{26}(t,p)\ Mg^{28}$ and the $Mg^{25}(t,\alpha)Na^{24}$ reactions. These, surprisingly, are superimposable. Studies underway intend to measure the range of recoil Mg^{28} atoms and to determine the relationship between the ground state spins of the products and the cross sections of their formation.

Milking Systems: Two of the recent milking systems developed are the Y^{89}-Sr^{87m} and the Mg^{28}-Al^{28} generators. Investigations underway include the development of generators for the Ti^{44}-Sc^{44}, Ar^{42}-K^{42}, and isomer generators of the Te isotopes, $Te^{127-131}$.

Miscellaneous: Carrier-free Fe^{52}, Cs^{129} and Cs^{132} are prepared by alpha bombardment of Cr^{50}, I^{127} and I^{129} respectively and are being made available for research. Unknown isotopes being searched for include Ti^{42}, Sc^{51}, Ca^{50} and K^{46-48}.

Publications

1. Hillman, "A Decay of Sc^{48}," Phys. Rev., 129, 2227 (1963).

2. Weiss and Hillman, "The Magnesium-28-Aluminum-28 System: An Aluminum-28 Generator," Intern. J. of Applied Radiation and Isotopes, in press

SECTION 4

HANFORD ATOMIC PRODUCTS OPERATION - HANFORD LABORATORIES

4-1 Chemistry in Molten Salts

4-2 Mechanisms of Solvent Extraction

4-3 Research Programs in Chemistry

For further information on work completed, the reader is referred to the open scientific literature.

4

HANFORD ATOMIC PRODUCTS OPERATION

Hanford Laboratories
Chemical Research

M. T. Walling, Jr./L. L. Burger

12/1/63

CHEMISTRY IN MOLTEN SALTS

The purpose of this work is to use molten salts as a medium to investigate molecular interactions, in particular the coordination chemistry of the actinide elements, in the absence of competition from the highly basic water molecule. A secondary aim is the development of methods and techniques suitable for high temperature manipulations and measurements. One of the principal areas of investigation is the electronic spectra of the actinides in various molten salt environments, including the assignments of observed transitions and the resolution of spectra into individual distribution curves. This phase of work is closely coordinated with other work in the laboratory, particularly determination of crystal structure and the comparison of spectra of the complexes in systems other than molten salts. The identification of ionic complexes in molten salt solutions is fundamental to the understanding of the coordination chemistry of the actinides and is one of the goals of the work.

Other areas of investigation involve solubility studies and the partition of elements between immiscible molten salt phases and other two-phase systems involving, for example, a molten salt as one phase - and a metal or organic compound as the other. Conventional physical properties are measured when pertinent.

It is felt that these studies - where there is no competition from the highly basic water molecule - will yield very significant information on the nature of bonding in complex ions of the actinide elements and possibly information more susceptible to interpretation on the basis of present day theory.

Publications

1. J. R. Morrey and R. H. Moore, "Thermodynamic Evidence for Complex Formation of Actinide Elements in Fused $KCl-AlCl_3$ Solvents," J. Phys. Chem. 67, No. 4, April (1963).

2. R. H. Moore, "The Immiscibility Gap in the System: $LiCl-KCl-AlCl_3$," J. Chem. Eng. Data, April (1963).

3. J. R. Morrey, E. E. Voiland, "Fused Salt Spectrophotometry II. The Effect of Black-Body and Sample Emission on Absorption Spectra," Spectrochim. Acta 18, 1175 (1962).

4. J. R. Morrey, "Fused Salt Spectrophotometry III. Isosbestic Points Generated by Variation in Temperature," J. Phys. Chem. 60, 2169 (1963).

HANFORD ATOMIC PRODUCTS OPERATION
Hanford Laboratories
Chemical Research

M. T. Walling, Jr./L. L. Burger
12/1/63

MECHANISMS OF SOLVENT EXTRACTION

The purpose of this work is to examine in detail the interaction of inorganic compounds with organic and inorganic solvents. Solvent extraction involves a number of different but related phenomena such as solvation of ions and of undissociated molecules, ion pair formation, hydrogen bonding, simple salt formation, and chelation as well as the weaker molecular interactions found in ordinary solutions.

The approach used is to employ techniques which are especially suited for the different phenomena. Ultraviolet and visible spectrophotometry are being employed to study the environmental effect of different ligands around, for example, an actinide element ion. Infrared and nuclear magnetic resonance are being employed to study general solvation phenomena and the nature and strengths of hydrogen bonds. Liquid-liquid partition data are used to obtain both thermodynamic and structural information on the complexes in solution. Among the solvents being used are ethers, neutral organophosphorus compounds and alkyl amines. Ion exchange studies are used in a similar fashion.

These studies are closely correlated with other programs in this laboratory, especially work with molten salt systems, crystallographic structure determinations and the interpretation of electronic spectra.

Publication

1. W. E. Keder and A. S. Wilson, "Amines as Extractants - Studies of the Organic Phase," Nucl. Science and Eng., 17, 287 (1963).

2. W. E. Keder, "Extraction of Tetra- and Hexavalent Actinides from Hydrochloric Acid by Tri-n-Octylamine in Xylene," J. Inorg. Nucl. Chem. 24, 561 (1962).

3. L. L. Burger, "Dialkyl Diethers in Solvent Extraction," J. Chem. Eng. Data, (Accepted for publication, January or February, 1964).

HANFORD ATOMIC PRODUCTS OPERATION

Hanford Laboratories
Chemical Research

M. T. Walling, Jr./L. L. Burger

12/1/63

RESEARCH PROGRAMS IN CHEMISTRY

The purpose of this work is to investigate the nature of chemical bonding in complexes formed by actinide elements in the various oxidation states obtainable in aqueous, organic, and molten salt solutions as well as in the solid state. Systematic measurement of the electronic spectra of solutions and their assignment to identified solution species has been in progress for some time, utilizing a variety of synthesis and phase partition techniques and a computer code developed for the mathematical treatment of the recorded spectra. A computer code for the interpretation of x-ray diffraction powder patterns (for cubic, hexagonal, and orthorhombic systems) has likewise been developed. Equipment for obtaining single crystal x-ray diffraction data is also being assembled and the determination of the crystal structure of compounds of interest to this study is underway, aimed at acquiring the information essential to the interpretation of the electronic spectra on the basis of crystal field theory. In addition to the foregoing basic tools, supplementary structural information is obtained via studies of the magnetic susceptibility, infra-red spectra, and nuclear magnetic resonance spectra. Further information on the nature of bonding in complexes and on symmetry can be obtained from Raman spectra and this technique may be added in future studies.

Publications

1. J. R. Morrey, "Fused Salt Spectrophotometry IV. Uranium(IV) in Chloride Melts", J. Inorg. Chem., 2, 163 (1963).

2. J. L. Ryan, "Anion Exchange and Non-Aqueous Studies of the Anionic Chloro Complexes of Hexavalent Actinides," J. Inorg. Chem., 2, 349 (1963).

3. J. L. Ryan, C. K. Jorgenson, "Electron Transfer and 5f-6d Transitions in Uranium(IV), Neptunium(IV), and Plutonium(IV) Hexahalides," Mol. Phys. 7, 17 (1963).

SECTION 5A

LAWRENCE RADIATION LABORATORY - BERKELEY

CHEMISTRY DIVISION

5A1 Studies of Alpha and Beta Decay Using Oriented Nuclei

5A2 External Field Nuclear Polarization

5A3 Investigations of the Internal Conversion Process in Nuclear Decay

5A4 Studies of Nuclear Level Schemes at High Precision

5A5 Bombardments of Cf With Various Heavy Ions

5A6 Neutron-Deficient Praseodymium Isotopes in a Region of Nuclear Deformation

5A7 Decay Schemes of Nuclei Near Double-Closed Shells

5A8 Nuclear Spectroscopic Investigations Near the Doubly Closed Shell of Pb^{208}

5A9 Nuclear Spectroscopic Measurements in the Transition Region Between Spherical and Strongly-Deformed Nuclei

5A10 Nuclear Spectroscopic Investigations of Deformed Heavy-Element Nuclides

5A11 Study of Alpha Emitters of Platinum and Nearby Elements Produced by Reactions of Complex Ions with Rare Earth Targets

5A12 Calorimetric Measurement of Decay Energy of Metastable U^{235}

5A13 Nuclear Spins, Moments, and Hyperfine Structures of Some Radioactive Isotopes

5A14 Calculation of Matrix Elements of Two-Nucleon Interactions in Nuclear Shell Theory

5A15 Theoretical Nuclear Structure Calculations

5A16 Measurement and Interpretation of Fission Barriers

5A17 Prompt Radiations in Fission

5A18 Spontaneous Fission

SECTION 5A Continued

5A19 Mass and Energy Distributions in Fission

5A20 Heavy Ion Fission Studies with Various Elements: Fission Fragment Kinetic Energy Measurements

5A21 Heavy Ion Fission Studies with Various Elements: Fission Cross Section Studies

5A22 Mass Spectrometric Study of Intermediate Energy Fission

5A23 Investigation of Range-Energy Relationships and Range Straggling Effects of Recoils from Heavy Ion Reactions

5A24 Investigation of Spallation, Fission, and Fragmentation Reactions by Radiochemical Techniques in Targets Bombarded with High Energy Protons, Deuterons, and Helium Ions

5A25 Investigation of the p-p Interaction Via the He^3(d,t)2p and He^3(p,d)2p Reactions

5A26 Polarization in p-p, p-d p-He^4 Scattering

5A27 Proton-Induced Two-Nucleon Pickup Reactions

5A28 Excitation of High-Spin Nuclear Levels by (α,d) Reaction

5A29 Mechanisms of Low Energy Nuclear Reactions of Protons, He^3, and He^4

5A30 Measurement of the Correlation Coefficient C_{NN} in p-p Scattering in the 30-57 MeV Range

5A31 Nuclear Reactions Induced by π Mesons

5A32 The (α,2α) Reaction on Several Elements in the 100 MeV Range

5A33 Study of Angular Correlation Between Inelastically Scattered Helium Ions and γ-Rays

5A34 Elastic and Inelastic Scattering of Charged Particles

5A35 In-Beam Spectroscopy Following Heavy Ion Reactions

5A36 Coulomb Excitation Using Heavy Ions

5A37 Theoretical Investigations of Direct Nuclear Reactions and Their Connection with Nuclear Structure

SECTION 5A Continued

5A38	Semiconductor Radiation Detectors
5A39	General Purpose Pulse Amplifying and Processing Equipment
5A40	Chemistry Instrument Systems
5A41	Crystal Structure Determinations
5A42	Crystal Structure Studies of Lanthanide and Actinide Compounds
5A43	Configuration Interaction in 1^N Configurations
5A44	Metastable Electronic States of Molecules
5A45	Multiply Charged Ions Formed by Electron Impact in the Mass Spectrometer
5A46	Molecular Beam Electric Resonance Spectroscopy
5A47	Studies of Induced Internal Fields in Ferromagnets
5A48	Mössbauer Effect Studies of Hyperfine Interactions and Lattice Dynamics
5A49	Xenon Chemistry
5A50	Ion Exchange and Solvent Extraction
5A51	Surface Ionization Studies
5A52	Paramagnetic Resonance Studies on Actinide Ions
5A53	Thermochemistry of the Lanthanide and Actinide Metals and Compounds
5A54	Preparation and Properties of the Transplutonium Metals
5A55	Solid State Spectra of Actinides
5A56	Free Atom Energy Levels of Actinides
5A57	Sensitive Activation Analysis for Oxygen, Carbon, and Other Elements by He^3-Induced Nuclear Reactions
5A58	Chemical Effects of Nuclear Transformations: Reactions of Recoil S^{35} and H^3 with Various Compounds

SECTION 5A Continued

5A59 Radiation Chemistry of Selected Organic Systems and the Role of Ions in the Radiolysis Process

5A60 Axial Mixing (Longitudinal Dispersion) in Packed Extraction and Absorption Columns

5A61 Kinetic Studies of Super-Acid Catalysis

5A62 Thermodynamics of Metal-Alloy and Fused-Salt Solutions

5A63 Mechanical and Chemical Properties of Nonequilibrium Liquid-Liquid Interfaces--Liquid-Solid Fluidization

5A64 Mechanical and Chemical Properties of Nonequilibrium Liquid-Liquid Interfaces--Studies with the Oscillating Jet

5A65 Liquid-Liquid and Gas-Liquid Agitation

5A66 Use of Atomic Hydrogen as a Possible Reducing Agent for Purification of Metals

5A67 Gas-Liquid Mass Transfer in Cocurrent Flow

5A68 Design of Liquid-Liquid Settlers

5A69 Bacterial Conversion of Inorganic Compounds

5A70 Turbulent Exchange of Momentum and Mass Between Fluid Streams and a Wall

5A71 Simultaneous Analyses of Elements Using Submilligram Amounts of Organic Samples

5A72 Optical Pumping Experiments in Neon and Mercury

5A73 Coherence Experiments with Laser Beams

5A74 Heat and Mass Transfer Between Fluid Phases

5A75 Oxygen Initiated Pyrolysis

5A76 Gas Liquid Mass Transfer

5A77 Basic Mechanisms in the Radiolysis of Amino Acids, Peptides and Related Compounds

For further information on completed work, the reader is referred to the Lawrence Radiation Laboratory, Berkeley, Chemistry Division Annual Report for the year ending December 31, 1963. It is report number UCRL-11213, February, 1964.

5A1

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

D. A. Shirley/R. B. Frankel/N. J. Stone 1/2/64

STUDIES OF ALPHA AND BETA DECAY USING ORIENTED NUCLEI

An important feature of charged-particle decay is the angular distribution, relative to the nuclear symmetry axis, of the emitted radiations . This distribution may be studied in an effective and straightforward manner by orienting the nuclei with respect to an external direction in space and observing the spatial anisotropy of alpha and beta particles, using semiconductor counters.

A program is underway to study, in this way, the angular distribution characteristics of alpha particles from heavy elements, particularly californium and einsteinium, and to elucidate some of the features of allowed and first-forbidden beta decay. To date these studies have shown that alpha particles are preferentially emitted from the poles of prolately deformed nuclei and have yielded unexpected information about the detailed shape of the angular distribution. Large "front-back" asymmetries have been observed in the beta decays of several isotopes and angular anisotropies have also been seen in the conversion electrons from oriented nuclei.

5A2

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

D. A. Shirley 1/2/64

EXTERNAL FIELD NUCLEAR POLARIZATION

The oldest, and conceptually the simplest, method for orienting nuclei in space to study their directional properties consists of polarizing the nuclei through interaction of the nuclear magnetic moments by means of an external magnetic field. In practice this method entails several severe experimental problems and in only a few isolated, favorable cases has it been applied successfully.

Because of the great potential value of external-field polarization, manifest particularly in its application to nuclear structure problems (including beta decay), a systematic long-range program to develop this method is underway. A number of preliminary and related experiments have been carried out and an apparatus has been designed and partially constructed. Arrangements have been made to use a 7 megawatt, 94,000 gauss magnet in the Low Temperature Laboratory of the University of California, Berkeley. Techniques have been developed for cooling radioactive samples to 0.01°K and for counting gamma rays in a magnetic field.

5A3

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

J. M. Hollander/T. Novakov 1/2/64

INVESTIGATIONS OF THE INTERNAL CONVERSION PROCESS IN NUCLEAR DECAY

The internal conversion coefficient, defined as the ratio of probabilities of atomic electron emission to photon emission in a transition between two nuclear levels, has been a quantity that the nuclear spectroscopist has found quite useful to measure. Largely, this is because the value of the conversion coefficient, according to theory, depends only on the angular momentum and parity changes involved (for a given transition) and is essentially independent of the details of nuclear structure. Thus one had a widely applicable tool for the measurement of these important quantities.

The situation was radically changed when some experiments showed that the I.C.C. (internal conversion coefficients) for some transitions deviated from the theoretical values. Theoretically these deviations have been described by considering the penetration of atomic electrons into the nuclear matter. The penetrating electrons "probe" the nuclear charges and transition currents, and can be in certain situations influenced by the details of the nuclear structure involved in a particular nuclear transition. Because of our knowledge of this effect, the I.C.C. have lost their sharpness as a tool for investigating the properties of nuclear states, but on the other hand careful experiments with conversion electrons can now provide information otherwise unobtainable.

We have studied a certain class of internally converted nuclear transitions, the L-subshell conversion of mixed M1-E2 transitions, using the Berkeley high-resolution 50-cm iron-free electron spectrometer. There is evidence from our preliminary results that this type of measurement may be a very sensitive tool for observing nuclear structure effects, and the program is being continued and expanded.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

J. M. Hollander 1/2/64

STUDIES OF NUCLEAR LEVEL SCHEMES AT HIGH PRECISION

With the installation at the Radiation Laboratory of a high-resolution iron-free beta spectrometer, it has become possible to investigate nuclear level schemes in greater detail than could previously be done at this laboratory. This instrument allows the measurement of internal conversion spectra with a precision approaching $1{:}10^5$, and an automatic scanning feature makes practical the realization also of high statistical accuracy.

A study of the decay of 20-day ${}_{99}Es^{253}$ was one of several that were carried out during the first year of operation, and it is illustrative of the type of investigation made possible by the iron-free spectrometer. The decay of Es^{253} gives rise to a number of energy levels in the daughter nucleus ${}_{97}Bk^{249}$, and the properties of sixteen of these levels have been investigated with high precision. Such properties include energies, intensitites, and quantum characteristics of the radiations that de-excite the excited levels. With the data, detailed correlations have been made of the observed properties with properties calculated from theoretical nuclear models, with use of presently-known nuclear interactions and forces. The objective of the program is to obtain sufficiently precise data that they can be used with confidence in developing further the nuclear theory.

5A5

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

A. Ghiorso/T. Sikkeland/A. E. Larsh/R. M. Latimer 1/2/64

BOMBARDMENTS OF Cf WITH VARIOUS HEAVY IONS

One of the objectives of this research is to discover elements 104 and 105. The research is done with special equipment during bombardment of californium with carbon and nitrogen ions. The equipment makes use of a combination of electrostatic and electromagnetic fields to separate short-lived recoiling atoms from the bombarding beam of ions.

Another aim of these experiments is to separate and identify new isotopes of the known heavy elements. This is being done mostly by chemical methods at the moment. A new technique is being employed involving volatilization of the recoils from a metal catcher foil followed by ion exchange separation and subsequent alpha particle pulse analysis. The relatively high vapor pressures of the heaviest element metals makes selective volatilization useful.

5A6

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

I. Perlman/J. E. Clarkson 1/2/64

NEUTRON-DEFICIENT PRASEODYMIUM ISOTOPES IN A REGION OF NUCLEAR DEFORMATION

The gamma spectra following the decay of the Praseodymium isotopes, Pr^{134}, Pr^{132}, Pr^{130}, are being investigated to determine first-excited state energies of the daughter nuclei or possibly to observe rotational band cascades. Such evidence could help determine the boundary of a new region of deformed nuclei.

In this work, $Pr^{134}(t_{1/2} = 17 \pm 2$ min.) was shown to have an $\frac{E_{(4+)}}{E_{(2+)}} =$ 2.53 whereas a rotational model would predict a value of 3.33. The value of the $E_{(2+)} = 0.415$ MeV, does not indicate deformation when compared to the value for $E_{2+(crit.)}$ used in demonstrating this property. Another isotope, $Pr^{132\pm1}$, ($t_{1/2} \sim 6$ min.) is currently being studied to determine similar ratios, and Pr^{130} will be studied if the half-life is of reasonable duration for investigation.

In the course of this work, Ce^{130} was observed to have $t_{1/2} = 25 \pm 2$ min. by following the growth and subsequent decay of the 0.360 MeV gamma ray in La^{130}.

Techniques involved are those of heavy ion bombardments at the HILAC on appropriate targets, fast chemical separations, and analysis of spectra by coincidence gamma ray spectroscopy.

5A7

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

J. O. Rasmussen/J. M. Hollander/J. A. Cooper 1/2/64

DECAY SCHEMES OF NUCLEI NEAR DOUBLE-CLOSED SHELLS

The energy level schemes of nuclei near double-closed shells are especially valuable for comparison with shell-model theoretical calculations. The level schemes of nuclei near Pb^{208} have already yielded much information on the proper force for shell-model calculations.

We are attempting to develop some energy level information on nuclei near Sn^{132} ($Z = 50$, $N = 82$) by studying decay schemes of short-lived fission products from a californium-252 spontaneous-fission source.

We are also studying level schemes of odd-odd nuclei near Zr^{90} (proton subshell 40, neutron shell 50).

5A8

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

I. Perlman/F. Asaro/R. Thoresen 1/2/64

NUCLEAR SPECTROSCOPIC INVESTIGATIONS NEAR THE DOUBLY CLOSED SHELL OF Pb^{208}

The purpose of this study is to enhance our knowledge of the nuclear forces and nuclear structure of presumably spherical nuclei. At the present stage many of the measurements involve the necessary preliminary identification of nuclear radiations. An example of the type of measurements is provided by the recently completed experiments on At^{204}, At^{206}, and At^{208}. By using different types of chemical and physical methods to separate astatine from polonium, we were able to show that previously-assigned longer-lived isomers of At^{208} (6 hours), At^{206} (2.7 hours) and probably At^{204} (25 minute) were illusions due to chemical effects.

The gamma ray singles and coincidence spectra of At^{205}, At^{206}, and Po^{205} have been investigated and partially interpreted. More detailed interpretation in terms of nuclear structure will be possible as additional measurements are made.

5A9

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

I. Perlman/V. Subrahmanyam/F. Asaro/D. Mosier 1/2/64

NUCLEAR SPECTROSCOPIC MEASUREMENTS IN THE TRANSITION REGION BETWEEN SPHERICAL AND STRONGLY-DEFORMED NUCLEI

Very little is presently known about the characteristics of nuclear energy levels for those nuclei in the transition region. Nuclei in this region are thought to be soft toward "vibrational" deformation from the spherical equilibrium shape. As part of the program of studying the nuclear forces in this region we have investigated the alpha decay schemes of Pa^{227} and Pa^{229}. One of the problems in this region is that the energy levels are very close together and can be resolved in many cases only with high-resolution equipment. We are able to cope with this by using one of our high resolution magnetic spectrographs as part of an alpha particle-gamma ray coincidence system. These alpha-particle and gamma-ray spectroscopic measurements have shown that odd-mass rotational bands (characteristic of strongly deformed nuclei) still appear in the transition region.

In addition to the states characteristic of the deformed region, other states have been found in this region. More and different types of spectroscopic measurements should enable us to further characterize these latter states in terms of nuclear structure.

LAWRENCE RADIATION LABORATORY - BERKELEY   Chemistry Division

I. Perlman/F. Asaro/F. Stephens/W. McHarris   1/2/64

NUCLEAR SPECTROSCOPIC INVESTIGATIONS OF DEFORMED HEAVY-ELEMENT NUCLIDES

The purpose of this investigation is to obtain a better understanding of nuclear structure and nuclear forces for those nuclei which have a permanent spherical deformation. The type of work can be illustrated by two investigations we have just completed--the alpha decay schemes of Fm^{255} and Es^{254m}. With our magnetic alpha-particle spectrographs and solid-state spectrometers we investigated the alpha spectrum of Fm^{255} and determined eleven energy levels of the daughter.

By various types of gamma-ray coincidence techniques we were able to study the quantum characteristics of these levels and show how they could all be described in terms of the Bohr-Mottelson and Nilsson theories for strongly deformed nuclei. The results were the first experimental measurement of the ordering of the energy levels above the neutron subshell of 152 neutrons.

Es^{254m} has the same number of neutrons as Fm^{255} (just discussed) and the same number of protons as Es^{253} (which we had investigated in previous years). The investigation of Es^{254m} was similar to that of Fm^{255}. It showed that all of the detected low-energy states could be described in terms of Fm^{255} and Es^{253} states. In addition many of the alpha-particle and gamma-ray decay characteristics of Es^{254m} could be described by similar characteristics of Fm^{255} or Es^{253}.

5A11

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

E. K. Hyde/A. Siivola 1/2/64

STUDY OF ALPHA EMITTERS OF PLATINUM AND NEARBY ELEMENTS PRODUCED BY REACTIONS OF COMPLEX IONS WITH RARE EARTH TARGETS

The Heavy Ion Linear Accelerator is an excellent accelerator for the production of nuclei on the neutron deficient side of beta stability. In the case of the interaction of C^{12}, 0^{16}, Ne^{20} and such nuclei with heavy nuclei of the rare-earth elements it is possible to prepare isotopes of platinum which are extremely deficient in neutrons. Such nuclei decay by electron capture with rather short half-lives but there may be competitive decay by alpha emission. It is the purpose of this investigation to gather as much information as possible about the alpha decay properties of these platinum isotopes.

This is being done by techniques worked out previously in this laboratory for the study of alpha emitters in the rare earth elements. The platinum isotope produced in the target is ejected from the target into an atmosphere of helium, where it is slowed down and then swept out of the target chamber to a counting chamber. There it is caught on a surface located near a semiconductor detector. This detector records the number and energy of the alpha particles emitted by the platinum products. The mass number is identified by the variation in yield as a function of the bombardment energy of the heavy ion.

5A12

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

H. P. Robinson/Barbara Bailey 1/2/64

CALORIMETRIC MEASUREMENT OF DECAY ENERGY OF METASTABLE U^{235}

The present work has been undertaken to resolve large discrepancies in measured values of the decay energy of U^{235m}. Values between 20 and 75 electron volts have been obtained by direct measurement of conversion electron energies. At these energies this measurement is difficult and subject to considerable uncertainty.

When U^{235m} is deposited on very small thermistor beads, virtually all the energy is converted to heat and transferred to the bead. The resultant temperature rise can be observed and measured as a change in the thermistor resistance in a sensitive Wheatstone Bridge circuit.

The U^{235m} will be chemically separated from approximately 7 grams of Pu^{239}, purified, and deposited on one of a pair of matched thermistors. About four half-lives will elapse before equilibrium conditions are reached in the calorimeter, so that a temperature rise of less than 0.001 degree is expected, corresponding to generation of 4×10^{-8} calorie per second.

The calorimeter has been built and is now undergoing extensive tests.

5A13

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

W. A. Nierenberg 1/2/64

NUCLEAR SPINS, MOMENTS, AND HYPERFINE STRUCTURES OF SOME RADIOACTIVE ISOTOPES

Present work by the atomic beam method includes a spin determination on Ce^{143}, magnetic hyperfine structure anomaly measurements on two isotopes of tungsten, a direct measurement of the magnetic moment of Pr^{142}, and the hyperfine structure of Pm^{148} and Er^{165}. Recently the spins of Gd^{153} and Pm^{148} were determined. Further work on the isotopes of rhenium is being started to determine the magnetic moments directly, and perhaps the hyperfine structure anomaly.

In addition, a mass spectrometer of the Pauli type is being tested; it will be used to detect stable isotopes, and allow additional hyperfine structure anomaly experiments to be performed.

5A14

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

M. G. Redlich 1/2/64

CALCULATION OF MATRIX ELEMENTS OF TWO-NUCLEON INTERACTIONS IN NUCLEAR SHELL THEORY

Calculations on the double-closed-shell core model have led generally to rough agreement with many data, especially energies, for nuclei with closed shells ± two or three particles. Usually the interaction V(1,2) between outer particles has been approximated by a scalar potential. For Bi^{210}, however, recent work has shown that a central + tensor interaction is needed to obtain this agreement. The purpose of the present investigation is to determine whether such agreement can be obtained with a specific central + tensor Yukawa interaction which accounts for the data on the two-nucleon system at low energies. A recent, very general method is used to calculate the matrix elements as sums of type $\sum c_m K_m$, where the K_m are simple integrals depending upon V(1,2), and the c_m will be calculated exactly on a computer, without any of the decimal approximations which may sometimes introduce considerable errors, using the new multiple-precision computer arithmetic.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

J. O. Rasmussen/N. K. Glendenning/H. J. Mang 1/2/64

THEORETICAL NUCLEAR STRUCTURE CALCULATIONS

Nuclear structure calculations are being carried out in a broad program making considerable use of the capabilities of the IBM-7094 computer at the Laboratory.

1) The most sophisticated residual-force mixtures including the tensor force are applied to nuclei 2, 3, or 4 nucleons removed from doubly-closed nuclei. Detailed comparisons with experimental spectra are made to try to make definitive determination of the residual shell-model force.

2) The many-body problems of spherical, single-closed shell nuclei are being attacked by the powerful variational techniques of the Bardeen-Cooper-Schrieffer (BCS) approach to superconductors. Binding energies, nuclear moments, radioactive transition rates, and spectroscopic factors for direct nuclear reactions are being extracted from theory to compare with experiment. Emphasis is currently on use of more realistic forces than hitherto employed in such calculations. The usually-neglected interactions between quasi-particles are also being investigated.

3) For the deformed nuclei the variational BCS methods are being applied with simple but more realistic forces than hitherto used, and really large systems are treated. The wave functions from fixed deformation are being applied to comprehensive alpha decay calculations. The variational formalism has been generalized to encompass self-consistent calculation of equilibrium deformations themselves under influence of finite-range residual forces. Nuclear surface deformations of higher order than quadrupole are being investigated theoretically.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

S. G. Thompson/W. Swiatecki/F. Plasil/A. Khodai 1/2/64

MEASUREMENT AND INTERPRETATION OF FISSION BARRIERS

Fission barriers are among the most basic of the predictions of a theory of fission. Since there is a scarcity of experimental data, particularly for the elements below radium, the first objective of this research is to obtain data from which accurate values of fission barriers may be deduced for a wide range of elements. The results may be compared with those calculated from theory and used to determine the extent of its validity. The related theoretical expressions and basic constants of the theory are consequently subject to confirmation and adjustment.

An example of a barrier measurement which has recently been completed is that of Tl^{201}, produced by the bombardment of Au^{197} with helium ions. A new technique involving the detection of fission fragments in mica was used to measure the fission cross section over a range of 10^{10}, the lowest value being approximately equal to $2 \times 10^{-35} cm^2$. A new theoretical expression which takes into account quantum mechanical barrier penetration was used to fit the data, deduce the fission barrier, and estimate the range of validity of the values of the penetration factor. These results made it possible to calculate more exact constants for the barrier formulae and for various mass formulae.

The research provides a foundation for the determination of the extent of the influence of angular momentum on the lowering of fission barriers. A certain amount of experimental data already obtained may now be interpreted and compared with theoretical results. Further research may also involve the measurement of angular distributions and studies of the nuclear level structure in the neighborhood of fission barriers.

5A17

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

S. G. Thompson/J. O. Rasmussen/H. R. Bowman 1/2/64

PROMPT RADIATIONS IN FISSION

This research involves the study of the prompt neutrons, gamma rays and other radiation associated with the primary fission process. One example has been in the detailed studies of the angular and energy distributions of neutrons from the spontaneous fission of Cf^{252}, where it was found that approximately 90% of the neutrons could be accounted for as being evaporated from moving fission fragments. The excitation energies of the fragments, and the neutron energy spectra were also determined as functions of fragment mass.

A second example is in the studies of the prompt gamma ray energy spectra as a function of fission fragment mass. In this case, discrete gamma ray peaks have been observed which are characteristic of certain masses and the observations of the Doppler shift in the energy of the radiation has aided in the identification of the masses. This research is in its beginning stages and has considerable application not only to the study of nuclear structure in a region of nuclides not available by other means, but also to the understanding of certain fission phenomena, such as the angular momentum of fission fragments and its dependence on fragment mass and energy. The methods are applicable to γ-ray lifetime measurements and the determination of angular distributions. The possibility exists for studying the X-rays and conversion electrons from prompt fission events as functions of fragment mass. Such information is of considerable interest in connection with the study of the primary nuclear charge distribution in fission.

As a refinement of the general approach described above, some new methods are being developed for simultaneous velocity and energy measurements of fission fragments. The velocity measurements involve the use of very fast tunnel diodes to obtain maximum speed in timing. By means of these methods, it may be possible to make very precise mass determinations.

5A18

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

S. G. Thompson 1/2/64

SPONTANEOUS FISSION

This research involves the study of trends in spontaneous fission half-lives, related systematics and other spontaneous fission properties which may eventually be understood in terms of a comprehensive theory of fission. One approach has been in the interpretation of half-lives in terms of the influence of the level structure on the passage of the nucleus through the fission barrier. On this basis, the half-lives of new very heavy nuclei have been predicted. The results indicate that a new region of nuclides having comparatively long half-lives may be approached for $Z > 102$, provided these nuclides have a sufficient neutron excess.

5A19

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

S. G. Thompson/F. Plasil 1/2/64

MASS AND ENERGY DISTRIBUTIONS IN FISSION

Studies of mass distributions in fission have long been subjects of major interest and speculation in fission research. The approach which has been taken here involves the simultaneous measurement of the energies of both fragments from fission events. The masses of the fragments are calculated directly from the energies. One example of such research was in measurements which were made on some rare isotopes undergoing spontaneous fission. Distributions in mass and energy were also studied for a wide range of nuclei produced by bombardments with particles ranging from helium ions to very heavy ions. These distributions are, therefore, obtained as functions of excitation energy and angular momentum of the fissioning nuclei. These results are directly comparable with the results of calculations on the basis of a new theory. The agreement is thus far surprisingly good and the measurement comparison will be extended over a wider range of elements to determine the extent of validity of the model, which is expected to apply, at this state, only to the elements below radium.

5A20

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

T. Sikkeland 1/2/64

HEAVY ION FISSION STUDIES WITH VARIOUS ELEMENTS: FISSION FRAGMENT KINETIC ENERGY MEASUREMENTS

The method used consists of very careful fragment-fragment angular correlation measurements in fission induced by heavy ions. One detector is at a permanent position at $\pi/2$ to the beam axis and the coincidence rate is measured as function of the position ψ of the other detector relative to the beam axis. At the peak of the correlation function the most probable intrinsic center-of-mass kinetic energy E_{cm} of the fragments is given by:

$$E_{cm} \quad (1-n_N/m_{CN})(0.25 + \tan^2\bar{\psi})P_I{}^2/m_{CN}.$$

Here n_N is the average number of neutrons emitted before fission, P_I the momentum of the ion, m_{CN} the mass of the compound nucleus and $\bar{\psi}$ the angle at which the coincidence rate is a maximum. The quantity n_N can be deduced from fission cross section measurements (see above). By comparison of the intrinsic laboratory energy at position $\bar{\psi}$ to the final laboratory energy as seen by the detector, the average number of neutrons N emitted from the fragments can be obtained by assuming the neutrons are evaporated. In previous angular correlation measurements the quantity $N\langle E\rangle$ has been evaluated where $\langle E\rangle$ is the average cm kinetic energy of the neutrons. Values for $\langle E\rangle$ can thus be obtained. The results will be compared to liquid drop model calculations and to reaction theories.

5A21

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

T. Sikkeland 1/2/64

HEAVY ION FISSION STUDIES WITH VARIOUS ELEMENTS: FISSION CROSS SECTION STUDIES

Fission excitation functions have been measured in reactions between O^{16} of varying energy and various targets ranging from Cs to Bi. In one set of experiments the same compound nucleus Re^{181} has been formed three ways by bombarding Tm, Ho, and Tb with C^{12}, O^{16}, and Ne^{22}, respectively. The data are now analyzed and values for fission barriers are being extracted. The results will be compared to liquid-drop-model calculations.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

M. C. Michel 1/2/64

MASS SPECTROMETRIC STUDY OF INTERMEDIATE ENERGY FISSION

The recent increase in interest, both experimental and theoretical, in the nature of the fission process has shown that a more detailed and precise knowledge of the process will be needed to allow any reasonable theoretical interpretation. The present program involves the use of direct mass-spectrometric measurement of appropriate fission product yields in order to achieve relatively high precision and freedom from the more common systematic errors inherent in the radiochemical approach. This type of data is of interest in itself and in conjunction with the energy and time-of-flight measurements recently made possible by new developments in experimental techniques.

Two types of yield measurement are included in this research. The chain yield data are of fundamental importance in any fission work and these data are relatively rare for intermediate energy fission. More precise and more widely spread chain yields are becoming of importance for comparison with prompt fragment data from coincident fragment energy and time-of-flight experiments in order to determine the neutron yield as a function of mass number. This may be a critical property in the attempt to distinguish between possible "Two mode" or "fragment shell" hypotheses. Apparently only the mass spectrometric method is sufficiently precise to offer serious hope for success with such treatment.

In addition, measurements of independent fission yields can lead to a knowledge of the charge distribution in fission and again, because of the limited number of possible yield measurements, high precision is very desirable to allow any detailed comparison of different fissioning systems.

Much work of both types has been completed and this has led to the demonstration that the charge distribution in fission has approximately the same properties from excitation energies of 6 to over 40 MeV, the observed shift in most probably A for a given chain being primarily or perhaps exclusively due to neutron evaporation from the fragments. Preliminary results also indicate an unexpected variation of neutron yield with mass number which is in quantitative agreement with the two mode hypothesis and with the results of Britt and Whetstone from coincident fragment energy and time-of-flight measurements.

Even more interesting work is now possible with lower Z elements where the transition to the more "symmetric" fission mode occur, and on the possible effect of the 50 proton shell on the fission process as predicted from the correct fragment shell treatments.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

E. K. Hyde/J. Gilat 1/2/64

INVESTIGATION OF RANGE-ENERGY RELATIONSHIPS AND RANGE STRAGGLING EFFECTS OF RECOILS FROM HEAVY ION REACTIONS

The range of an energetic charged particle in matter is a matter of considerable importance to physics because the energy of such a particle must often be computed from its distance of travel in some stopping medium. It is also important to understand the rearrangement of electronic structures of the charged particle as it slows down. There are great gaps in our knowledge of range-energy relationships, particularly for large ions traveling at many MeV or tens of MeV energy.

The Heavy Ion Linear Accelerator is a useful source of complex nuclei of known energy for new studies of range-energy relations. There is a large class of products which are known to be the result of complete amalgamation of the incoming projectile (C^{12}, O^{16}, Ne^{20}, etc.) with a heavy target nucleus followed by the evaporation of a few neutrons. The heavy product nucleus is formed with a known energy.

The range of this heavy product in a series of target foils can be measured by radiochemical techniques. Alternatively, a gas-filled stopping chamber can be used.

A number of such studies are being carried out particularly for energetic nuclei of rare earth elements.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

E. K. Hyde/W. Treytl/D. Sisson 1/2/64

INVESTIGATION OF SPALLATION, FISSION, AND FRAGMENTATION REACTIONS BY RADIOCHEMICAL TECHNIQUES IN TARGETS BOMBARDED WITH HIGH ENERGY PROTONS, DEUTERONS, AND HELIUM IONS

The particle beams available for this project are the 6.4 GeV protons from the bevatron, the 730 MeV proton, 700 MeV deuteron and 880 MeV helium ion beams from the 184 inch cyclotron, and the 50 MeV proton and 100 MeV helium ion beams from the 88 inch cyclotron. The deuteron and helium ion beams of the 184 inch cyclotron provide an almost unique capability since only one other accelerator in the world (a Russian cyclotron) provides these projectiles at these high energies.

The goal of the program is to study radioactive products from targets representative of all regions of the Periodic Chart and to learn as much as possible about the mechanism of interaction of high energy particles with complex nuclei. The yield of the products are measured as a function of energy, and the recoil properties of selected products are investigated. The chief mechanism of high energy reactions is believed to be a 2-step process consisting of a fast cascade of quasi-free collisions between the incoming projectile and the individual nucleons in the nucleus and a slow de-excitation by particle evaporation and fission. The experimental results served as a test of the mechanism and as a means of determining the parameters in calculations relating to the two steps. High energy fission reactions can be fitted into the 2-step reaction mechanism but there are many factors of high energy fission which are distinctly different from low energy fission.

It is known that some products of high energy reaction cannot be accounted for by the conventional model of high energy reactions and must be the results of a fast, violent disruption of the nucleus called fragmentation. A major purpose of the program is to obtain more information on the nature of fragmentation.

5A25

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

H. E. Conzett/R. J. Slobodrian/S. Yamabe 1/2/64

INVESTIGATION OF THE p-p INTERACTION VIA THE $He^3(d,t)2p$ AND $He^3(p,d)2p$ REACTIONS

Information on the p-p interaction can be gained by analysis of the energy spectra of tritons and/or deuterons from the respective reactions $He^3(d,t)2p$ and/or $He^3(p,d)2p$. For example, in the (d,t) reaction a peaking of tritons near the maximum triton energy could be due to the influence of an unbound state of the 2p system; thus, from the triton spectra, information on this 2p state can be derived.

5A26

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

H. E. Conzett/R. J. Slobodrian/S. Yamabe 1/2/64

POLARIZATION IN p-p, p-d, p-He^4 SCATTERING

A polarized proton beam of variable energy up to 60 MeV is being developed by making use of the large polarization induced in p-α scattering. The beam intensity will be of the order of 10^8 protons per second with a polarization of 80-100% over the available energy range.

Initial experiments will then investigate the polarization induced in p-p, p-d and p-He^4 scattering. Since little information of this sort is available at energies between 15 and 100 MeV, these experiments are important to the development of an understanding of the basic nucleon-nucleon and few-body problems.

5A27

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

J. Cerny/R. H. Pehl 1/2/64

PROTON-INDUCED TWO-NUCLEON PICKUP REACTIONS

The variable energy proton beam (20 to 50 MeV) available at the new 88-inch cyclotron at Berkeley permits the investigation of both the (p,t) and (p,He^3) reactions, neither of which have been previously studied to any appreciable extent.

The (p,t) experiments such as $C^{12}(p,t)C^{10}$ enable one to investigate the energy levels of nuclei that cannot be studied by most of the commonly used nuclear reactions. In addition, preliminary results on the even-even target nuclei C^{12}, 0^{16}, and Ca^{40} indicate that the mechanism of the (p,t) reaction may be sufficiently simple to enable theory to establish the spins and parities of these levels. Particular nuclei whose levels schemes are poorly or not known and which can be readily reached by (p,t) reactions include C^{10}, Mg^{22}, Si^{26}, Ar^{34}, and Ca^{38}.

Studies of (p,He^3) reactions can be carried out simultaneously with the (p,t) experiments using a new particle identifier developed by F. S. Goulding. It is hoped that the investigation of (p,He^3) reactions will remove the ambiguity in the interpretation of the mechanism of (d,α) reactions, in which a p-n pair is also transferred. The (d,α) reactions can proceed by pick-up or, in the cluster model approach, by knock-out, while the (p,He^3) reaction should proceed in first order solely by pick-up. Comparison of (p,He^3) data on certain transitions to previous (d,α) data should clarify the situation.

Furthermore, there are several pairs of transitions in which (in isobaric-spin formalism) a (p,t) and a (p,He^3) reaction proceeds on the same nucleus to the same final state, e.g., the $0^{16}(p,t)0^{14}_{g.s.}$ (0+, T = 1) and the $0^{16}(p,He^3)N^{14*}$ (2.31 MeV, 0+, T = 1) transitions. Since these transitions possess identical initial and final states, except for Coulomb energy differences, one would expect to find that the individual angular distributions could be fit by the same optical potentials in a two-particle D.W.B.A. calculation. Precise measurements of the (p,t) to (p,He^3) transition ratio to these states will be obtained to check this assumption which may also serve as a check on the completeness of the optical potentials used in these analyses.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

J. Cerny/B. G. Harvey/R. H. Pehl 1/2/64

EXCITATION OF HIGH-SPIN NUCLEAR LEVELS BY (α,d) REACTION

Studies of the (α,d) reaction on light elements at the Crocker Laboratory's 60-inch cyclotron showed that only certain excited states of the product nuclei are strongly populated in this two-particle transfer reaction. The strongly populated states were found to be those in which the captured proton and neutron enter the $d_{5/2}$ shell, coupling their angular momenta to the maximum value of 5. The "core" of the nucleus is left unchanged in the reaction. For example, the spin-5 level of F^{18} at 1.1 MeV is very strongly excited by $O^{16}(\alpha,d)F^{18}$. Immediately preceeding the final demolition of the Crocker Cyclotron, it was found that the $J = 7$ level of the configuration $(f_{7/2})^2$ is very strongly excited in Sc^{42} by the reaction $Ca^{40}(\alpha,d)Sc^{42}$.

Reconstruction of the equipment at the 88-inch cyclotron is now complete. Preliminary tests show that far better energy resolution can be obtained at the cyclotron. Studies of the $(f_{7/2})^2$ $J = 7$ configuration will continue.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

S. S. Markowitz/A. J. Pape/C. F. Smith 1/2/64

MECHANISMS OF LOW ENERGY NUCLEAR REACTIONS OF PROTONS, He^3, AND He^4

Research is in progress to test compound-nucleus theory. One project tests, in a manner similar to that of Ghoshal, whether a compound nucleus such as Zn^{64*}, formed by different nuclear reactions of protons, He^3, and He^4, on the proper copper and nickel target nuclides, will decay independent of its mode of formation. Excitation functions are being determined for different radioactive products of the nuclear reactions mentioned.

To study possible "alpha-particle clustering" within nuclear matter and "direct" interactions, a program is being carried out to measure the cross section and recoil behavior of $_4Be^7$ nuclei formed by the reaction of $_2He^3$ ions with various target nuclides. The addition, possibly by a direct "pickup" mechanism, of an alpha particle, $_2He^4$, to the He^3 projectile as the He^3 passes near or through the nuclear surface region, should give information on alpha clustering. To compare and test the hypothesis, cross sections for Be^7 formation from He^4 projectiles with different target nuclides are also being studied. Because of the different binding energies of He^3 and He^4 species, it is postulated that He^4 direct pickup should be more probable than He^3 direct pickup to form the same Be^7 product. The possible formation of the Be^7 by evaporation is also being considered.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

George Igo/P. Darriulat/H. Pugh

MEASUREMENT OF THE CORRELATION COEFFICIENT C_{NN} IN p-p SCATTERING IN THE 30-57 MeV RANGE

The availability from the 88-inch cyclotron of intense (up to 10 μA) proton beams of energies as high as 57 MeV with good duty cycle characteristics makes it possible to measure the spin correlation coefficient C_{NN} (E_p)* in the proton energy range E_p = 30-57 MeV with a far higher accuracy than previously obtained in the single measurement that exists at present in this energy range.

In the measurement, a 0.1" thick moving strip of polyethylene acts as a proton target and is bombarded with a proton beam. The unscattered portion of the proton beam is refocused by a quadrupole triplet onto a shielded Faraday cup twenty feet away where the beam energy, intensity, and position may be monitored.

Scattered and recoil protons produced in a p-p scattering event at $90^\circ \pm 1^\circ$ in the 0.1" thick polyethylene foil will pass into a pair of polarimeters with an intensity of 5×10^5 sec^{-1}. In the polarimeters, the protons strike carbon targets from which they may be rescattered into counters placed at 45°, left and right. The expected count rate for detecting an event where both protons are rescattered into polarimeter counters is on the order of 1 count/15 sec. Consequently good statistical accuracy may be obtained in a day's running time.

The quantity actually measured in the experiment is $\langle P_A \rangle \langle P_B \rangle C_{NN}$ (E_p) where $\langle P_A \rangle$ and $\langle P_B \rangle$ are the analyzing powers of the polarimeters; $\langle P_A \rangle$ and $\langle P_B \rangle$ are to be determined by placing the polarimeters in a highly polarized proton beam ($P \simeq 0.99 \pm 0.01$) and measuring the asymmetries with P positive and with P negative.

---

* L. Wolfenstein, Am. Rev. Nucl. Sci. 6, 43 (1956).

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

Samuel S. Markowitz/Paul Reeder/David Anderson 1/2/64

NUCLEAR REACTIONS INDUCED BY π MESONS

The interaction of π mesons with nuclear matter is being studied to understand the mechanism involved. The Berkeley 184-inch synchrocyclotron is used to provide a beam of pions sufficiently intense (about 10^6 pions per minute) to give measurable amounts of radioactivities.

The immediate goal of the work with the pions is to compare the "simple" reactions, such as $(\pi,\pi n)$ with those already studied at high energies such as (p,pn). The first cross-section measurements at different pion energies were those with C^{12} as the target. Work is continuing with other light elements and with more complex reactions.

The excitation function for the reaction $C^{12}(\pi^-,\pi^-n)C^{11}$ was measured from 53 to 1610 MeV by bombarding targets of plastic scintillator with pions. The intensity of the pion beam was monitored with a two-counter telescope and 40-Mc scaling system. The scintillator target was mounted on a phototube and became the detector for the C^{11} positron activity. Corrections were made for muon contamination in the beam, coincidence losses in the monitor system, C^{11} activity produced by stray background at the accelerator, C^{11} activity produced by secondaries in the target, and the efficiency of the C^{11} detection system.

The $C^{12}(\pi^-,\pi^-n)C^{11}$ cross sections rise from a threshold at about 50 MeV to a peak of about 70 mb at 190 MeV after which they decrease to 30 mb at 373 MeV and are relatively constant at higher energies. The (π^-,π^-n) peak occurs at the same energy as the resonance in free-particle π^-n scattering at 190 MeV. Calculations based on a "knock-on collision" mechanism and "sharp cutoff" nuclear density reproduce the shape of the experimental excitation function, but the magnitudes of the calculated cross sections are low by a factor of about 5 or 6. This simple model indicates that the $C^{12}(\pi^-,\pi^-n)C^{11}$ reaction occurs in the nuclear surface region at all bombarding energies.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

George Igo/P. Darriulat/H. Pugh 1/2/64

THE (α, 2α) REACTION ON SEVERAL ELEMENTS IN THE 100 MeV RANGE

With the availability of intense alpha particle beams of good duty cycle up to an energy of 130 MeV, it becomes possible to study the (α,2α) reaction in greater detail than before. Previous studies at lower energies ($<$ 50 MeV) or at very high energy (930 MeV) have indicated the desirability of 1) increasing the energy above 50 MeV so that, for light elements, the level density at the excitation energy of the compound nucleus, if it is formed at all, will be very dense and thus the reaction will be "direct" -- a direct knockout process rather than a two stage process, 2) increasing the energy above 50 MeV for heavy elements so that the outgoing alpha particle reaction products will not be inhibited by Coulomb barrier effects, and 3) decreasing the energy well below 930 MeV in order to obtain the necessary energy resolution to separate out reactions involving specific excited states of the residual nucleus.

We have measured the basic (α,He^4) cross section as a function of angle and energy. From this data, plotted as a contour diagram, suitable regions may be located where the cross section does not change too rapidly with either angle or energy, a desirable situation to have for the (α,2α) reaction. Necessary adaptation in the counter and scattering chamber design to obtain the optimum geometry are in process, and the initial state of research will concentrate on light alpha particle-like nuclei.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

B. G. Harvey/J. R. Meriwether/D. J. Horen 1/2/64

STUDY OF ANGULAR CORRELATION BETWEEN INELASTICALLY SCATTERED HELIUM IONS AND γ-RAYS

The γ-ray decay of the 4.43 MeV, 2+ state of C^{12} in coincidence with the inelastically scattered α particles populating this state has been studied using 40 MeV α particles. This work showed marked deviation from the prediction of the simple Blair adiabatic approximation. The deviation can be seen in the variation of θ_0, the symmetry angle of the γ-ray angular distribution, as a function of the α particle detection angle. The theory predicts a straight-line relation, but one finds a variation which is reminiscent of a tangent function. It is supposed that the adiabatic approximation becomes more applicable as the bombarding energy is increased. For this reason it is proposed that the $(\alpha,\alpha'\gamma)$ reaction on C^{12} be studied as a function of energy. The 88-inch cyclotron is particularly applicable to such a study, as it provides a wide variation in bombarding energy. In addition, its high and uniform duty cycle facilitates coincidence measurements.

In addition it is proposed that an octopole excitation be studied for comparison with the quadrupole excitation described above. The 3- level at 6.137 MeV in O^{16} will provide a good experimental example for this case. It is one of the few examples of a nuclide where the 3- state decays exclusively to the ground state and not to some intermediate state.

Such experiments should provide rather sensitive tests of the theories of inelastic alpha scattering. Furthermore, they will provide general information which can be applied to other particle gamma ray correlations, such as $(\alpha,d\gamma)$.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

B. G. Harvey/H. E. Conzett/G. J. Igo/J. R. Meriwether 1/2/64

ELASTIC AND INELASTIC SCATTERING OF CHARGED PARTICLES

The study of the scattering of particles has always been an important source of information about the nucleus. (In fact the existence of the atomic nucleus was discovered as a result of such experiments). The availability of high energy charged particle beams from accelerators led to a vast increase in experiments of this type during the 1950's.

The 88-inch cyclotron is specially suitable for scattering experiments since it makes available to the experimenter beams of several different particles at a variety of energies. The use of a beam energy-analysis system, combined with detection of scattered particles by high resolution silicon counters, permits the experimenter to observe the excitation of large numbers of nuclear excited states. To make full use of the new possibilities afforded by the 88-inch cyclotron, several groups are studying the elastic and inelastic scattering of (mainly helium) ions in a series of separate but related experiments.

These experiments emphasize different aspects of the scattering process: a) An experimentally measured angular distribution can be analyzed in terms of partial-wave phase shifts. Hopefully, the phase shifts can be correlated in terms of relatively simple quantities of real physical interest such as the nuclear radius and the diffuseness of the nuclear surface.

b) The elastic and inelastic differential cross sections may be interpreted by means of the <u>nuclear optical model</u>. Previous alpha particle scattering has been done at a lower energy range (<50 MeV). The higher energies now available make more extensive tests possible, and in addition, with the availability of a well defined beam, better energy resolution and more precise measuring gear, better defined data may be obtained.

c) Since many excited nuclear states can be observed by energy analysis of the scattered beam, such experiments become of great value to <u>nuclear spectroscopy</u>. In this case, very good energy resolution is of prime importance but there is usually less interest in the measurement of very precise angular distributions.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

F. S. Stephens/R. M. Diamond/J. Burde 1/2/64

IN-BEAM SPECTROSCOPY FOLLOWING HEAVY ION REACTIONS

Work already performed here and at other laboratories has demonstrated the great capabilities of in-beam nuclear spectroscopy. Isomers and radioactivities with half-lives in the millisecond to minutes region can be studied very cleanly by conversion-electron and gamma-ray spectrometers in the off-duty cycle of pulsed accelerators such as the Berkeley HILAC (3 msec pulse, 6-20 times per second). Microsecond isomers and radioactivities can be similarly studied by pulsing the beam at this shorter time scale. Finally, the prompt transitions in the gamma-ray cascades following nuclear reactions can be studied if the number of types of reactions produced can be limited by the proper choice of conditions. The use of heavy-ion projectiles allows a greater choice of such conditions and of suitable reaction products than is possible with just protons or alphas, and the much greater amount of angular momentum imparted to the compound nucleus also has interesting consequences.

We plan to continue the present program of investigating millisecond isomers, as in the study of the light thallium isotopes, and to extend it to the microsecond region. We are studying the in-beam gamma-ray cascades in even-even nuclei which are the final steps in the production of these nuclei from various heavy-ion reactions. Considerable information on the levels in the rotational region (Ytterbium, Hafnium, and Tungsten isotopes) has been obtained and is being prepared for publication. More work on such rotational nuclei is planned, and in particular this type of study seems to be very promising for looking at the new regions of deformation. Nuclei in the vibrational region, (Osmium, Platinum, Mercury) are being studied now, and to confirm the decay schemes and spin assignments proposed, more elaborate coincidence experiments are planned.

Publication

1. Diamond and Stephens, "Isomeric Levels in the Light Thallium Isotopes," Nucl. Phys. 45, 632 (1963).

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

R. M. Diamond/F. S. Stephens 1/2/64

COULOMB EXCITATION USING HEAVY IONS

Heavy ions have been shown to have some distinct advantages over light projectiles for Coulomb excitation studies. The most important of these is the increased probability for causing a given excitation. This means that many states can be excited directly from the ground state in sufficient intensity for study, whereas with light projectiles the intensity is not sufficient. Even more important, it means that states can be excited by multiple processes which cannot otherwise be reached by any direct process. We are currently making use of the large number of states so excited in studying the systematics of levels in odd-mass deformed nuclei. The collective states, because of their enhanced transition probabilities, are preferentially populated, and our interest has been directed primarily at the vibrational states in such nuclei. Several nuclei have already been studied (Tb^{159}, Ho^{165}, and Tm^{169}), one is in progress now (U^{235}), and we anticipate studying several more (Re^{185}, Re^{187}, Ta^{181}, Lu^{175}, and perhaps Pu^{239}) in the reasonably near future.

A closely related study is that of even-even deformed nuclei. We have essentially completed work on two such nuclei (U^{238} and Th^{232}) and here the collective states are almost the only ones populated. The three lowest-lying vibrational bands (K values of 0+, 2+ and 1-) are prominently observed in both nuclei. We plan to extend these studies in the heaviest elements (Th^{230}, U^{236}, and U^{234}) and perhaps eventually into the rare earth deformed region.

A very interesting subject for such studies will be the spherical even-even nuclei; and, particularly in conjunction with our in-beam nuclear-reaction spectroscopy program, we plan to initiate some studies of this type in the next year. The separated platinum isotopes have been obtained for this purpose. There is presently little known about the levels in this type of nucleus, and we anticipate that most of our effort in the next year may be directed toward accumulating information on such levels.

Publication

1. Diamond, Elbeck, and Stephens, "Coulomb Excitation of Tb^{159}, Ho^{165}, and Tm^{169} with O^{16} Ions," Nucl. Phys. 43, 560 (1963).

5A37

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

N. K. Glendenning 1/2/64

THEORETICAL INVESTIGATIONS OF DIRECT NUCLEAR REACTIONS AND THEIR CONNECTION WITH NUCLEAR STRUCTURE

The theory of two-nucleon stripping or pickup reactions has been developed in such a way as to give a central role to the structure of the nuclear states involved. These reactions are particularly suited to the study of certain correlations in the nuclear wave function of the two transferred nucleons. In heavier nuclei they are probably also sensitive to coherent mixtures in the wave function that are induced by pairing matrix elements of the residual (shell model) interaction. The appropriate correlations and coherence are properties of only a few states in any nucleus and this gives rise to the large fluctuations in cross section to the various states, observed in experiments. An analysis of the experiments by the present methods, in conjunction with nuclear structure calculations, therefore can lead to assignments of spin parity, and configuration to the strongly excited states, some of which lie at quite high excitation. It also provides a check on the structure calculations.

5A38

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

W. L. Hansen/F. S. Goulding 1/2/64

SEMICONDUCTOR RADIATION DETECTORS

Investigations in this area have covered all aspects of the techniques associated with manufacturing α, β, and γ detectors of all types, the theory of the devices and the electronic-noise theories necessary for an understanding of the fundamental limitations on resolution in energy measurements.

For high-resolution work with α and β particles, our emphasis has hitherto been upon phosphorous-diffused silicon junction diodes. In order to avoid the ambient sensitivity of the devices - due to surface effects - we have developed a technique for the passivation of the detector surface by producing a high temperature oxide on the silicon surface. While this technique is similar in general to that used in making planar transistors, the high resistivity of the bulk material used in counters necessitates studies of and compensation for the electrical layer normally produced at the $Si\text{-}SiO_2$ interface. Detectors made by this process show α-energy resolutions as low as 13 keV (full width at half maximum).

Lithium-drifted silicon detectors are employed where thick depletion layers are required to stop particles (e.g., energetic β's, α's, p's, etc.). The drifting process is well understood but again the detector surface at the edge of the Li-Si junction and at the opposite face when the lithium drifts right through the device present problems. Various "potting" techniques to reduce surface problems (the SiO_2 technique cannot be used due to the need for low temperature processing) have been tried and experience so far indicates that a silicon varnish or rubber may reduce surface problems at the junction edge. A technique has been developed to measure the approach of the drifted region to the back face of the wafer. This technique permits termination of the drift process just before the drifted region reaches the back face. Thus, over-drifting may be prevented.

Lithium-drifted germanium detectors for high resolution γ-ray spectrometry are being made in appreciable quantities. The drifting process is similar to that used in silicon but currents during drift are very large. In order to drift thick detectors without thermal runaway, automatic control of drifting is being attempted at the present time. These detectors are used at liquid nitrogen temperature and the design of detector mountings and the handling of detectors requires much ingenuity.

LAWRENCE RADIATION LABORATORY - BERKELEY		Chemistry Division

F. S. Goulding/D. Landis/L. B. Robinson		1/2/64

GENERAL PURPOSE PULSE AMPLIFYING AND PROCESSING EQUIPMENT

As a result of a program to develop a series of functional circuit blocks which find common use in many coincidence and amplitude spectrometry application, a very versatile transistorized linear amplifier and gating system was developed and is now in use. Specific functional units which form parts of this system will also be available as separate modules. These include:

1. Linear Amplifier - gain X 1000; rise time - 90 ns.
2. Low-Noise Preamplifiers for use with solid-state detectors.
3. A Scintillation Preamplifier.
4. Linear Gate - Speed ∼ 100 nsec; Pedestal etc. - 10 mV.
5. Biased Amplifier - linear for signals 10 mV over bias level.
6. Output Shaper - shapes a 1.5 μsec square pulse from any input normally encountered. This allows use of optimum time constants to give best resolution and provides a signal suitable for Pulse-Height Analyzers.

Over twenty of the amplifiers are in use with no failures observed in several of these over a period of six months.

One unusual application of this system has been to select scintillation pulses from phototube noise by recognizing the difference in pulse shape. By using a good phototube we have measured a 5.9 keV x-ray with a resolution of 48% with noise counts above 2 keV totaling less than 1 per minute.

Units not mentioned in the above list permit use of two of the systems to carry out fast-slow coincidence experiments. The time resolution may be adjusted from 10 to 110 nsec and the pulse crossover system employed gives timing accuracies of about 5 nsec over a 50:1 range of signals of the typical NaI-Tl shape, (i.e., 0.3 μsec time constant).

The testing of this system and pulse-amplitude analyzers required an accurate technique for measuring differential linearity. For this purpose, a generator of pulses whose amplitude increases linearly with time was developed. This unit, which will generate random or equally spaced pulses, permits testing the differential linearity of a system quite accurately. The ramp linearity is believed to be better than 0.25% but this is so much better than pulse measuring systems that no good measurement of the pulser linearity has been made.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

M. Nakamura 1/2/64

CHEMISTRY INSTRUMENT SYSTEMS

Various specific instrumentation projects associated with research programs in the Nuclear Chemistry Division have been undertaken. Examples include:

(1) The scanning and recording of spectrum lines on spectrographic plates. A commercial optical comparator will be used for measuring the spectrum lines. We are building the electronics for digitally recording the position and the intensity of the spectrum lines. The precision of the comparator is good to one micron. The comparator carriage can measure distances of over 10 inches in one scan. It is capable of accommodating spectrographic plates of 18 inches.

(2) The study of measurement techniques for fission fragment traces made in mica sheets: Mica sheets discriminate against all but the most heavily ionizing particles, making mica useful for counting fission fragments with no interference from other charged particles.

(3) Work has also been carried out on two techniques for stabilizing the calibration of amplifier and analyzer. The first is an analog stabilization scheme by which a single channel analyzer baseline is modulated around a photopeak, and gain shifts are sensed in the usual manner. The gain-shift correction signal is fed into a low-level amplifier whose gain can be changed electrically by this correction signal. The second is a digital stabilization scheme similar to the type first described by J. Ladd of Chalk River. We have adapted this scheme to simultaneously stabilize the gain of four parameters being recorded in our multi-parameter recording system. The correction signals for gain shifts are fed to low-level amplifiers in a manner similar to that of the analog stabilization scheme.

5A41

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

D. H. Templeton/A. Zalkin/J. D. Forrester 1/2/64

CRYSTAL STRUCTURE DETERMINATIONS

In this research, x-ray diffraction techniques are used to determine the structures of crystals of a wide variety of substances. Some crystals are chosen for study on the basis that their structures may reveal principles of the geometry of atomic arrangement or the nature of the chemical bonding. In other cases new compounds are identified by determination of the crystal structure. The structures of molecules, including the details of distances and bond angles, are determined when these molecules exist in the crystal. Some crystals are investigated because it is important or useful to know their structures for the interpretation of other kinds of physical or chemical investigations of their properties. Other aspects of this research are improvement of (a) the procedures for measurement of the x-ray intensities, (b) the mathematical methods involved in the interpretation of the data, and (c) the facilities for making diffraction measurements at low temperatures.

5A42

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

B. B. Cunningham/J. C. Wallmann/J. Green/B. M. L. Bansal 1/2/64

CRYSTAL STRUCTURE STUDIES OF LANTHANIDE AND ACTINIDE COMPOUNDS

Crystallographic characterization of important compounds, especially oxides and halides, is a continuing project which is automatically extended to include new elements in this series as they become available. Recent work has included precise lattice measurements and thermal expansion coefficient measurements of $PuCl_3$, $AmCl_3$, $CmCl_3$; structural identification and unit-cell size determination of BkO_2, and crystallographic identification of PmF_3.

Preliminary work has been done on $BkCl_3$, BkOCl, $CfCl_3$, and CfOCl, but not with samples of purity adequate for precise measurements.

Measurements with highly purified materials are planned for the near future and an attempt will be made to extend the crystallographic work to Einsteinium.

5A43

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

Katheryn Rajnak 1/2/64

CONFIGURATION INTERACTION IN ℓ^N CONFIGURATIONS

A general theoretical study of the empirical analysis of the atomic spectra of ℓ^N-type configurations has been undertaken. It has been shown that considerable amounts of configuration interaction are already included (to second-order in perturbation theory) in the usual fitting of Slater parameters and spin-orbit coupling constants. The origin of the "linear effects" of configuration interaction has been clarified and the formulation of non-linear effects carried out. With the proper choice of parameters (17 for f^N configurations) all configuration interaction may now be accounted for (in second-order perturbation theory).

Present efforts are directed toward applying the theory to the spectrum of Pr III and other specific cases where sufficient data are available. By fitting several different spectra one should gain a feel for the behavior of the new configuration interaction parameters as a function of atomic number and degree of ionization. It should then be possible to interpolate at least some of them to provide a guide to the analysis of other lanthanide and actinide spectra where less data is available.

Configuration interaction via spin-orbit and electrostatically correlated spin-orbit interactions has also been considered in the same light and theoretical work has begun on other electrostatically correlated magnetic interactions. The effect of crystal fields is also being considered.

Publications

1. Rajnak and Wybourne, "Configuration Interaction Effects in ℓ^N Configurations," Phys. Rev. Oct. 1, 1963, <u>132</u>, 280.

2. Rajnak and Wybourne, "Electrostatically Correlated Spin-Orbit Interactions in ℓ^N-type Configurations," Phys. Rev. (to be published).

5A44

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

K. Street, Jr./A. S. Newton/John Olmsted III 1/2/64

METASTABLE ELECTRONIC STATES OF MOLECULES

The formation of metastable states of molecules, i.e., triplet states formed by electron impact, is being studied by a molecular beam method. Such states, which have lowest levels below the lowest singlet state and are normally forbidden in optical excitation, can be formed using low energy electrons by an electron-exchange mechanism. The appearance potential, excitation function, and cross section for formation represent the goals of the study of these metastable states.

5A45

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

A. S. Newton/A. F. Sciamanna 1/2/64

MULTIPLY CHARGED IONS FORMED BY ELECTRON IMPACT IN THE MASS SPECTROMETER

A study is being made of the occurrence, stability, and appearance potentials of multiply charged ions formed from molecular species by electron impact in the mass spectrometer. Metastable states of such molecules and metastable transitions of the type, $M^{++} \rightarrow A^{+} + B^{+}$, where $A \neq B$, will also be studied. One example of this latter reaction already studied is the metastable transtion

$$CO_2^{++} \rightarrow CO^{+} + O^{+}$$

which has a half-life of 2.2 μsecs. Modifications in our mass spectrometer are being made which will allow the study of such metastable transitions in any volatile organic molecule.

5A46

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

K. Street/A. Hebert/W. Breivogel/C. Hollowell/T. Story 1/2/64

MOLECULAR BEAM ELECTRIC RESONANCE SPECTROSCOPY

This research was undertaken to study the electrical properties and nuclear-molecular interactions in simple molecules, and to apply this information to the understanding of molecular geometry and chemical bonding. At present the principal method of investigation consists of the study of microwave rotational spectra and radio-frequency Stark spectra of molecules by the molecular-beam electric-resonance method. These measurements give information on the rotational constants, dipole moment, molecular-nuclear quadrupole interaction, spin-orbit interaction, and spin-spin interaction. In contrast to the magnetic resonance method which averages hyperfine effects over rotational states, the electric resonance method gives these interactions for individual vibrational and rotational states.

The molecular beam apparatus now in operation consists of a differentially-pumped four-chamber high-vacuum system, high-temperature-oven source, tungsten ribbon surface ionization detector with a 5 cm radius permanent magnet mass analyzer and electron multiplier, inhomogeneous (two wire analog) electric deflecting fields, and a 30 cm long electric Stark field region that is homogeneous to approximately one part in 10^5.

The accuracy of the data obtainable with this apparatus exceeds in many cases the accuracy of previously available methods (low order perturbation theory) of theoretical treatment. Considerable effort is being expended in improving the treatment and programming the procedures used to analyze spectra in order to take advantage of these more accurate data.

The spectra of a number of alkali halide molecules have been obtained, e.g., Li^6F^{19}, Li^7F^{19}, Li^6Br^{81}, Li^6I^{127}, etc. The objective here is to fill in missing data on the alkali halides and increase the accuracy of previous work where this seems warranted. It is anticipated that the study of diatomic molecules will continue. Experiments on polyatomic molecules, both linear and non-linear are beginning.

5A47

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

D. A. Shirley/H. H. Wickman 1/2/64

STUDIES OF INDUCED INTERNAL FIELDS IN FERROMAGNETS

One of the best probes for studying the mechanism responsible for collective magnetism is the determination of the internal magnetic fields at nuclei of magnetic atoms. These fields arise from several interactions and their interpretation is seldom straightforward. When nonmagnetic atoms are dissolved in magnetic metals, however, only one or two of these interactions is operative, and measurements of the internal magnetic fields induced on the impurity atoms can provide unique information on these interactions.

Systematic studies are being made using nuclear polarization, angular correlation of nuclear gamma rays, and Mössbauer spectroscopy, to determine the variation of induced fields on nonmagnetic impurity atoms throughtout the Periodic Table. Results obtained thus far on the Group IB metals indicate that the internal fields are correlated with hyperfine field interactions and with the magnetic moments of the host, and that the dominant mechanism is either conduction electron polarization, or less likely, polarization of the atomic core.

5A48

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

D. A. Shirley/H. H. Wickman/R. B. Frankel/M. A. Faltens 1/2/64

MOSSBAUER EFFECT STUDIES OF HYPERFINE INTERACTIONS AND LATTICE DYNAMICS

The Mössbauer effect provides a method of measuring gamma-ray energies with very high precision. The resonant gamma rays can be used to detect very subtle chemical effects by measuring the hyperfine splittings and energy shifts arising from these effects. We are interested in using internal magnetic fields, quadrupole coupling constants, and chemical shifts to study the electronic configurations in compounds and alloys of several elements, particularly europium, gold, and the heavy rare earths and refractories. Studies to date have shown that there is a large amount of electron transfer in gold alloys and that europous salts have a modest covalent bonding. Both of these results are unexpected on the basis of currently accepted theories.

5A49

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

C. W. Koch 1/2/64

XENON CHEMISTRY

It is planned to continue the investigation of the chemistry ot xenon with particular emphasis on those species stable in aqueous solution. At the present time our work is concerned with the mechanism for the disproportionation of Xe(VI) in several strong bases. The mechanism appears to depend upon the specific base employed. From this study we hope to learn more about the stabilities of Xe(II) and Xe(IV) in aqueous solution and to extend the work to the hydrolysis of XeF_4 and XeF_2 in acidic as well as alkaline solutions. The rates of several reactions investigated are sufficiently slow that kinetic studies are in order. We have completed a rate study for the reaction between $XeO_3(aq)$ and Br^- in acid solution. It is planned to do additional research on the reaction between $XeO_3(aq)$ and I^- in dilute acid, $XeO_3(aq)$ and HO_2^- in strong base, Na_4XeO_6 and HO_2^- in strong base, and to investigate the disproportionation of $XeO_3(s)$ in strong base more quantitatively.

5A50

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

R. M. Diamond/A. Beck/J. Bucher 1/2/64

ION EXCHANGE AND SOLVENT EXTRACTION

Considerable progress has been made in understanding the ion-exchange resin elution behavior and selectivity orders of simple tracer cations and anions in dilute-to-concentrated solutions of several aqueous electrolytes. The results have been explained as a competition among water molecules, the resin groups, and the macro-electrolyte ion (of opposite charge to the tracer ion of interest) to solvate the tracer ion. An extension of these studies to non-aqueous solutions, or rather to mixed aqueous-organic solvent solutions is planned. Also, comparable studies with liquid ion exchangers, such as dinonylnaphthalene sulfonic acid, have been started.

The investigation of the solvent extraction behavior of strong acids with various extractants will be extended to less basic extractants, in the hope of observing the hydration of the extracting hydronium ion to the tri-solvated, $H_9O_4^+$, species. With the better extracting agents, such as the amines, the behavior of complex metalo-acids will be studied. The solvation of other ions, anions as well as cations, will be studied by the methods already used for the hydrogen and hydroxide ions; work on fluoride ion is already underway. It is hoped to also study these systems by NMR spectroscopy to better define the part water plays in the extracting complex.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

F. L. Reynolds 1/2/64

SURFACE IONIZATION STUDIES

High temperature metal surfaces and mass spectroscopy techniques are employed to study surface ionization and to make ionization potential and work function measurements. Previous reports on this work have contributed to values for the ionization potential of uranium and neodymium and to values for the work function of polycrystalline tungsten, rhenium, and tantalum. On single-crystal tungsten, work function values for the (110) plane and the (111) plane have been determined. This work also has practical application in improved surface-ion sources for mass spectroscopy and in basic research in ion-engine studies. Of added interest are the possible chemical reactions of both the metal surface and impinging atomic beam atoms with oxygen, nitrogen, and fluorine at these high temperatures, and the influence of these elements on the thermionic properties of the metal surface.

Of special interest is the use of the above technique in the determination of first ionization potentials of some of the actinide and rare-earth elements. Equipment is now being constructed to facilitate this study.

Publication

1. "Ionization on Tungsten Single-Crystal Surfaces," J. Chem. Phys. **39**, 1107 (1963).

5A52

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

B. B. Cunningham/M. Abraham 1/2/64

PARAMAGNETIC RESONANCE STUDIES ON ACTINIDE IONS

The low-lying electronic energy levels of various actinide ions in a lanthanum trichloride, or other crystalline matrix are being investigated by the paramagnetic resonance technique. To date it has been shown that in both lanthanum trichloride and lanthanum ethyl sulfate containing Cm^{+3} only a single resonance line is observed at liquid helium temperature. The observed line is attributed to a transition within the lowest doublet of the ground level $^8S_{7/2}$.

Owing to the high degree of intermediate coupling in the 5f elements, as compared with the 4f, crystal field splittings of the ground level are larger than kT at helium temperatures, accounting for the appearance of a single resonance line rather than seven lines as observed with Gd^{+3}.

It is hoped that it will be possible to investigate the isoelectronic Am^{+2} ion, but to date conditions have not been found for the preparation of a suitable sample.

5A53

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

B. B. Cunningham/J. C. Wallmann/J. Burnett 1/2/64

THERMOCHEMISTRY OF THE LANTHANIDE AND ACTINIDE METALS AND COMPOUNDS

The program is a continuing one designed to provide basic thermodynamic data on the transplutonium elements, and on selected lanthanide elements especially standard heats and free energies of formation of the aqueous ions.

To date data have been obtained for the ion Am^{+3}, Am^{+4}, AmO_2^{+}, AmO_2^{+4} and Cm^{+3}, based on microcalorimetric heat-of-solution measurements.

Currently measurements of the heats of formation of Eu^{+2}, Eu^{+3}, and EuO are being carried out. These results indicate serious errors in the literature values for the heats of formation of Eu^{+2} and Eu^{+3}.

The measurements will be extended as soon as possible to include Cm^{+4}, Bk^{+3}, Bk^{+4}, and Cf^{+3}.

5A54

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

B. B. Cunningham/J. C. Wallmann/J. Green/J. Burnett 1/2/64

PREPARATION AND PROPERTIES OF THE TRANSPLUTONIUM METALS

A program of preparation and study of the transplutonium metals is being carried out for the purpose of clarifying the question of metallic valences in this region of the periodic table. Major emphasis is being placed on structure determinations, solid-phase transformations and magnetic properties, but the program includes melting-point and vapor-pressure measurements as well. To date metallic americium and curium have been shown to exist at room temperature in a double hexagonal closest packed structure. The metallic radii of curium and americium are quite similar, and magnetic measurements indicate a metallic valence of 3.0 ± 0.2 in both metals.

Studies of metallic berkelium and californium are projected for the near future.

5A55

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

J. G. Conway/R. D. McLaughlin/A. Nichol 1/2/64

SOLID STATE SPECTRA OF ACTINIDES

The spectra of the actinides are observed by doping the actinides into single crystals of $LaCl_3$. In this crystal all the actinides are observed to fluoresce, and the highly radioactive ones such as Pu and beyond show a radioluminescence. This type of experiment together with the usual polarized absorption and Zeeman experiments has given valuable information about the 5f electrons and their interactions with the crystal fields. To date Pu(IV) and Am(IV) have been analyzed and the theoretical calculations carried out. This work gives a good understanding of these ions in the solid. Work is at present going on with Cm(IV) and U(IV). The work on U(V) was finished some time ago.

LAWRENCE RADIATION LABORATORY - BERKELEY   Chemistry Division

J. G. Conway/R. D. McLaughlin/G. V. Shalimoff/E. F. Worden/ 1/2/64
R. G. Gutmacher

FREE ATOM ENERGY LEVELS OF ACTINIDES

We are presently involved in the work necessary to determine the energy levels of actinides. Work is in progress on Cm(I) and Cm(II) and on Dy(I) which is in preparation for the planned experiments on Cf(I). Also the spectra of U(IV) and U(V) are being observed in emission. Work on At(I) is also being carried on. In the cases of Cm and Dy the line lists are in preparation. Each element has on the order of 9000 lines to its spectrum. These lines are measured to an accuracy of 0.001 A. Whenever possible, single isotopes are used. It is necessary also to separate spectra according to the degree of ionization. This is now possible with electrode lamps by varying the operation of the tube.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

S. S. Markowitz/J. D. Mahony 1/2/64

SENSITIVE ACTIVATION ANALYSIS FOR OXYGEN, CARBON, AND OTHER ELEMENTS BY He^3-INDUCED NUCLEAR REACTIONS

A simple, rapid, and general analytical method is being developed based upon nuclear reactions induced by low-energy He^3 ions. The sensitivity is fractions of a part per billion, and the precision and accuracy are about 5% at present. Microgram to milligram samples are sufficient and the sample need not be destroyed. The method is especially useful to determine those elements (for example, O, C, N, and F) that are difficult to determine at low sensitivity by conventional techniques or by neutron activation analysis.

The key feature is the use of He^3 ions accelerated to comparatively low kinetic energies. The He^3 nucleus has a very low binding energy of 7.7 MeV (compared with 28.3 MeV for He^4). Therefore many of its simple nuclear reactions are exoergic; once the Coulomb barrier is exceeded the cross sections are large. In addition to the thermodynamic benefits, the resulting radioactivities are mainly neutron-deficient and are positron emitters; this enables one to detect either the positrons by conventional beta counters or their annihilation radiation, singly or in coincidence, by NaI scintillation spectroscopy.

Interferences can be eliminated or minimized by choice of He^3 beam energy, reaction product, detection of radioactivity, and by rapid chemical separation if necessary.

The present research was carried out with the use of the Berkeley Hilac. Experiments using the $O^{16}(He^3,p)F^{18}$ reaction, for example, indicate that the maximum cross section of about 400 mb is at 7.5 MeV. Therefore, a small cyclotron (about 8 MeV for He^3 ions) would suffice to accelerate the He^3 that could be employed to analyze for any element up to calcium, $Z = 20$, where 8 MeV is the Coulomb barrier for He^3. Such a cyclotron would be only 9 inches in radius.

The effects of trace materials on transistors, biological samples, surfaces, and other solid-state devices are often profound. The He^3 analysis method is an effective tool for determining many trace elements in various matrices.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

S. S. Markowitz/M. L. Hyder/J. B. Nash 1/2/64

CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATIONS: REACTIONS OF RECOIL S^{35} AND H^3 WITH VARIOUS COMPOUNDS

To understand the mechanism of the reactions of "hot" atoms or ions with various molecules two approaches have been made. One is to produce a "hot atom," such as S^{35}, via the $S^{34}(n,\gamma)S^{35}$ reaction with thermal neutrons from a reactor and gaseous sulfur compounds. The other approach is to attempt to produce a beam of low-energy (many eV) ions and atoms such as H^3, which will strike a molecule such as CH_4 or C_2H_6, and then separate by gas chromatography the various tritiated products. The latter method is just being started. The $S^{34}(n,\gamma)S^{35}$ introductory work has been completed.

The chemical behavior of recoil S^{35} has been studied in gaseous H_2S, SO_2, SF_6, CH_3SH, and thiophene. The gasses were irradiated with thermal neutrons at the Livermore Pool-Type Reactor (LPTR). Among the effects studied were those of pressure, surface area, and additive gasses including argon, nitric oxide, hydrogen, and oxygen. The results are consistent with a model in which the original molecule is broken up in the nuclear recoil process and the resulting fragments containing S^{35} react with the surroundings only after they have been slowed to thermal energies; in general, the final chemical form of the S^{35} is determined by the chemical environment in which it is produced rather than by its original chemical form or oxidation state. However, irradiations of mixtures of several gasses with NO gave results possibly indicating that the chemical form of the S^{35} immediately after molecular disruption may depend upon the nature of the original molecule.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

A. S. Newton/A. F. Sciamanna 1/2/64

RADIATION CHEMISTRY OF SELECTED ORGANIC SYSTEMS AND THE ROLE OF IONS IN THE RADIOLYSIS PROCESS

A continuing study of the radiation chemistry of organic systems with special emphasis on the role of ions in such studies is being made. Systems of compounds such as alcohols, ethers, and the symmetrical dichlorethylenes have been studied in the past. Isovaleric acid, where a large molecular rearrangement occurs in the mass spectrum of the compound, is at present under study, with evidence that in the radiolysis of the gas phase such a rearrangement occurs but in the radiolysis of the liquid phase the rearrangement either does not occur or is small. Other molecules exhibiting large mass spectrometer rearrangement peaks will also be studied.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

T. Vermeulen/A. N. Hennico/J. S. Moon 1/2/64

AXIAL MIXING (LONGITUDINAL DISPERSION) IN PACKED EXTRACTION AND ABSORPTION COLUMNS

Experimental studies of liquid phase dispersion are being continued, both in single phase flow and in countercurrent liquid-liquid operation. This work is being extended to include the case of pulsed operation, as a means of gaining additional insight into the fluid mechanical characteristics of dispersion, and also in order to evaluate the value of pulsing in a possible improvement of packed-column performance. Efforts are being made to correlate the observed variation in Peclet number (relative to unpulsed operation) as the amplitude and frequency of pulsing increase. It is also planned to measure internal concentration profiles under actual gas-absorption operation in order to verify the applicability of the theory and the parameters already obtained.

Extending the work of Jacques and Cotter in this laboratory, in liquid-liquid systems, the continuous phase Peclet number may fall to one-tenth, or less, of the single phase value at high values of the velocity ratio. By contrast, relatively high (and nearly constant) values are obtained for the dispersed phase Peclet numbers, whether or not the dispersed phase wets the packing. For both phases, pulsed operation gives a higher Peclet number than unpulsed. General correlations are still lacking, and physical variables such as viscosity and interfacial tension have not yet been studied.

A series of actual extraction runs have been made in the experimental columns, using di-isobutyl ketone and water with acetic acid as solute; and isododecane-water, with crotonic acid. The latter system has also been run with pulsing. Analysis of these runs is still underway. In general they confirm the dispersion coefficient values measured in unsteady state runs, along with the method of analysis. This experimental study of extraction is regarded as incomplete, and is scheduled to be continued during the coming year.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

T. Vermeulen/J. Gmitro/R. Miller 1/2/64

KINETIC STUDIES OF SUPER-ACID CATALYSIS

This study has two longer term objectives: to determine the catalytic properties of near-anhydrous sulfuric, perchloric, phosphoric, acetic, nitric, and similar acids; and to develop the interrelations between mass transfer and chemical kinetics that apply in different contacting arrangements where acid catalysis is used. An intermediate objective is the development and analysis of a vapor phase apparatus for nitration of aromatic hydrocarbons.

As a basic step toward the thermodynamic description of mixed acid systems, the vapor pressure behavior of aqueous sulfuric acid solutions (in terms of water, H_2SO_4, and SO_3 as the vapor constituents) has been evaluated from 0 to 100 percent H_2SO_4 and from -50° to $+400^\circ C$.

In aromatic nitration, the active intermediate species is believed to be the nitronium (NO_2^+) ion, whose concentration depends upon the relative thermodynamic activity of free protons (H^+) in the system. The relative rates of nitration have been determined by others for a limited range of HNO_3 and H_2SO_4 mole fractions. These measurements are now being extended to cover practically the entire range of possible mixture compositions, using different aromatic compounds that will undergo nitration at reasonable rates at temperatures near $50^\circ C$. Meta-di (trifluoromethyl) benzene is being used as the aromatic feed in the concentrated-acid region, and nitro-benzene will also be studied in the next lower rate-range.

5A62

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

T. Vermeulen/H. Otsuki 1/2/64

THERMODYNAMICS OF METAL-ALLOY AND FUSED-SALT SOLUTIONS

A systematic study is being made to develop methods of predicting the solubility, diffusivity, electrical and thermal conductivity, and heat of mixing of liquid-metal mixtures from known properties of the pure metals in liquid form. The interaction of electrons with metal cations contributes to most of the mixture properties; its effects are not particularly susceptible to theoretical calculation, but it appears that theoretically sound statistical correlations can be reached between each property and a suitably weighted combination of other properties.

5A63

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

T. Vermeulen/J. A. Saxton 1/2/64

MECHANICAL AND CHEMICAL PROPERTIES OF NONEQUILIBRIUM LIQUID-LIQUID INTERFACES--LIQUID-SOLID FLUIDIZATION

A water-fluidized bed of uniform glass spheres, and of mixtures of different sizes of glass and/or plastic spheres is being used to study the following measurable properties: viscosity, surface tension, diffusivity, and miscibility behavior. The kinetic theory of liquids in simplified form is being applied to such systems, based on the analogy that each spherical particle is the counterpart of a single molecule of a true liquid. The gravitational force exerted upon the particle in the fluidized bed is the analog of an attractive force between particles, and the drag by the fluidized medium is analogous to a repulsive force between the particles.

In cases where the fluidized particles separate into two layers, the boundary between them is expected to provide an analog for the interface between two ordinary immiscible liquid phases. It is hoped to observe the magnitude and nature to both mechanical and mass transfer effects upon interface behavior, so as to provide a valuable adjunct to statistical mechanical calculation methods and to macroscopic measurements and observations on true liquid systems.

5A64

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

T. Vermeulen/A. E. Vandegrift 1/2/64

MECHANICAL AND CHEMICAL PROPERTIES OF NONEQUILIBRIUM LIQUID-LIQUID INTERFACES--STUDIES WITH THE OSCILLATING JET

The oscillating jet formed by flow through an elliptical nozzle or orifice has been investigated as a means of measuring dynamic interfacial tension in the 0.01 to 0.1 second time range. The interfacial tension varies with interface concentration of a transferring solute; the variation can be calibrated in separate equilibrium experiments. During mass transfer from the jet liquid to the surrounding liquid, or vice versa, a change in interfacial tension will be indicated by a variation in the wave length between successive nodes of the jet. An initial phase of the study has just been completed and a second phase will be started soon with the aim of improving the precision of the experimental techniques.

In the initial state, the mathematical behavior of the liquid-liquid system has been solved for the first time, with the aid of computer calculations; the exact solution previously available, developed by Bohr in 1909, applies only to liquid-gas systems. It was also necessary to solve for the radial velocity distribution within the jet, treating it approximately as being circular in cross section. These calculations are now undergoing further refinement preparatory to publication.

On the experimental side, about six satisfactory nozzles have been found (in the 1 to 2mm. size range, from capillary glass tubing) out of more than 200 made and tested. The apparatus that has been constructed and operated has been found relatively satisfactory for equilibrium measurements, but gives jets too short to be suitable for the dynamic studies. In this apparatus, the jet is injected into a stationary second phase. In future studies it is planned to have the outside phase moving in streamline flow at essentially the same velocity as the jet.

5A65

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

T. Vermeulen/M. W. Clark/T. D. Coughlen 1/2/64

LIQUID-LIQUID AND GAS-LIQUID AGITATION

Power requirements have been measured in the turbulent flow region for a series of rectangularly shaped vessels. The power number values for these experiments proved to lie between the baffled and unbaffled values for a cylindrical tank using the impeller.

Studies are currently underway to relate gas holdup to an impeller type in speed and gas flowrate. Further, power consumption is being determined as a function of these variables. An abrupt decline in the power number is observed with both increasing flow rate and increasing impeller speed. It is believed that the results of this study will aid in re-interpreting previous measurements of mean bubble diameter. The results are expected to apply to various types of absorption, extraction, and chemical reaction equipment.

5A66

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

D. N. Hanson/P. Rony 1/2/64

USE OF ATOMIC HYDROGEN AS A POSSIBLE REDUCING AGENT FOR PURIFICATION OF METALS

Atomic hydrogen is a possible reducing agent for removal of small amounts of oxygen from metals, in order to improve the ductility or other properties of the metal. Beryllium is an example. The brittle characteristics of beryllium in its presently available purity (100 ppm oxygen) are generally attributed to the residual oxygen. Chemical reducing agents, such as Ca, are not usable to remove this. Atomic hydrogen could remove the oxygen if recombination were not too rapid on the beryllium surface; available information on recombination rates at metallic surfaces indicates that recombination at the solid surface would be too rapid. However, no information is available on recombination rates at liquid surfaces. Since the metal to be reduced must be molten in order to provide reasonable transport of the oxygen to the surface, the recombination rate on liquid surfaces is important. The research under way at present is directed toward measurement of the recombination of atomic hydrogen on solid and liquid mercury surfaces.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

C. R. Wilke/C. J. King/J. Heuss 1/2/64

GAS-LIQUID MASS TRANSFER IN COCURRENT FLOW

The rate of mass transfer in gas-liquid systems is largely influenced by the amount of interfacial area present between the gas and liquid phases. For this reason industrial gas-liquid mass transfer devices generally contain packing of divided solids or are composed of sieve or bubble-cap plates which serve to provide a large interfacial area. In certain regimes of cocurrent two phase conduit flow it is also possible to achieve large interfacial areas per unit volume, but without the necessity of interposed solids. The result can be a more compact and inexpensive device. Although many studies have been made of pressure drops and factors influencing the type of cocurrent gas-liquid flow in a pipe, studies of mass transfer between gas and liquid phases are almost wholly non-existent.

In this project continuous flow test sections have been constructed of lucite pipe. Experiments involving the desorption of oxygen from water into air and the absorption of ammonia from air into water are being carried out to ascertain the gas and liquid phase resistances to mass transfer. The flow is maintained in the emulsification or bubble regime where the gas and liquid phases form a uniform froth rather than being stratified. The effects of both gas and liquid flow rates on the mass transfer are being determined.

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

C. R. Wilke/W. Sweeney 1/2/64

DESIGN OF LIQUID-LIQUID SETTLERS

This is a continuation of previous studies at this laboratory reported by Graham (UCRL-10048) and Epstein (UCRL-10625). The general objective is development of correlations and design methods for gravitational settlers for separation of immiscible liquids such as may be encountered in solvent extraction by mixer-settlers and direct contact heat transfer.

The present study involves separation of Arochlor (tetrachlorodiphenyl) and water in a rectangular vessel 4 feet in length X 6 in. wide X 12 in. high. A photoelectric probe is being developed to characterize the state of the dispersion entering the settler. Efforts will be directed to determining the effects of the entrance section design and mixing Reynolds number on the dispersion, and to determining effects of settler geometry and flow velocities under equivalent dispersion conditions.

5A69

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

C. R. Wilke/V. Edwards/D. Sortland 1/2/64

BACTERIAL CONVERSION OF INORGANIC COMPOUNDS

This project is a continuation of the work reported in the thesis by Leban*. The program is aimed at establishing general design principles for bacterial reactors with particular reference to inorganic systems.

Batch studies have been completed on reduction of sulfate ion to hydrogen sulfide with Desulfovibrio. A pure strain of bacteria has been isolated and rate data have been obtained to establish general magnitudes and the effects of the various reactants on the kinetics of sulfate production. Adaption experiments are in progress to develop strains which are active in high sodium chloride concentrations of 18% or more. Apparatus for continuous culture experiments is under construction to gain more accurate knowledge of the rate determining variables. The process may have application in purification of brines. Plant design studies are in progress to assess possible practical applications.

Future work in the program will include separation techniques for bacteria and related problems associated with development of reactors of minimum volume. Use of microorganisms for isotope separations and concentration of ionic species from dilute solutions will be considered in future studies.

*UCRL-10966

5A70

LAWRENCE RATIATION LABORATORY - BERKELEY Chemistry Division

C. R. Wilke/D. T. Wasan/R. M. Davis 1/2/64

TURBULENT EXCHANGE OF MOMENTUM AND MASS BETWEEN FLUID STREAMS AND A WALL

The turbulent exchange of momentum and mass (or heat) in the vicinity of a boundary is encountered in several engineering processes. Many studies have been made of the turbulent transfer rates by measuring the gross properties of a forced convection diffusion system, but a considerable discrepancy has been found in the experimental results due to inaccuracy in measurements and poor definition of the exact conditions of the problem. It is noted that the measurement of the gross properties of a forced convection diffusion system does not give an insight into the fundamental mechanism of mass transfer into turbulent flows. For this reason, this research is undertaken to develop a more basic approach to the study of turbulent exchange of momentum and mass between fluid and a wall in several ways:

1. Theoretical expressions have been developed to describe the variation of mean velocity and eddy diffusivity in the vicinity of a pipe wall. Furthermore, using these distributions, new correlations* have been derived to describe mass and heat transfer to a fluid in a fully developed turbulent flow in a pipe.

2. The turbulent rates of momentum and mass transfer to gaseous streams flowing normal to single cylinders are being investigated and a new correlation is obtained for the psychrometric ratio.

3. Mathematical solutions to a forced convection diffusion system are being obtained for the first time for the gas phase mass transfer in a cylindrical tube with constant concentration wall condition. Through the numerical solutions of the diffusion convection equation, the effect of the non-diffusing species concentration, the variation of Schmidt and Reynolds numbers and the entry length on the gas phase mass transfer coefficient are being investigated.

4. The experimental program involves the measurements of mean velocity and concentration distributions in turbulent flow of air through a porous ceramic pipe with mass transfer occurring from the wall to the gas stream. Experiments involving the vaporization of water into air are being carried out to ascertain the gas phase mass transfer rates. It is believed that from these results it will be possible to determine the effect of the mass transfer flux on the velocity distribution and the limitations of the theoretical analysis.

---

*Wasan and Wilke, UCRL-10556, March, 1963.

5A71

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

C. W. Koch 3/10/64

SIMULTANEOUS ANALYSES OF ELEMENTS USING SUBMILLIGRAM AMOUNTS OF ORGANIC SAMPLES

The determination of submilligram amount of the elements commonly present in organic compounds is being investigated employing vacuum techniques. The simultaneous determination of carbon, hydrogen and nitrogen has been successfully scaled down so that 200-500 μg samples are now routinely analyzed with an accuracy equivalent to that generally obtained for 5-20 mg samples (±0.2%). The present procedure is being extended further to include sulfur. Work also is in progress to reduce the size of the vacuum system so that amounts of organic substance required may be decreased to 20-50 μgs without appreciable loss of accuracy.

5A72

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

D. McColm/T. Hadeishi/I. Maleh/O. McHarris 3/10/64

OPTICAL PUMPING EXPERIMENTS IN NEON AND MERCURY

Experiments to detect low frequency rf resonances in both short-lived and metastable levels in neon are in progress. Electron-bombardment of neon gas is employed to populate the desired energy states; the spontaneously emitted light is observed.

In addition, an experiment is being performed on Hg^{203} with the aim of measuring its nuclear magnetic moment. Optical pumping is used as the polarizing technique.

5A73

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

D. McColm 3/10/64

COHERENCE EXPERIMENTS WITH LASER BEAMS

A study is being performed on the beam of a helium neon CW laser to determine its coherence properties. Special emphasis is to be placed on observing higher order correlations between the photons. Coincidence techniques are employed; photomultipliers are used as photon detectors.

5A74

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

C. J. King/C. H. Byers 3/10/64

HEAT AND MASS TRANSFER BETWEEN FLUID PHASES

The fundamental nature of heat and mass transfer between two immiscible fluid phases is being examined by means of both theoretical analysis and laboratory experimentation. The laboratory work is focussed upon flow situations where both of the phases present a significant resistance to the transfer processes. Of particular interest are cases (1) where heat and mass transfer occur simultaneously, (2) where there are relatively steep gradients in temperature and/or concentration, and (3) where various side effects enter, such as those caused by surface tension as density driven mixing processes. Initial investigations are concerned with smooth, laminar flow.

5A75

LAWRENCE RADIATION LABORATORY - BERKELEY Chemistry Division

C. J. King/E. D. Hausman 3/10/64

OXYGEN INITIATED PYROLYSIS

The effect of trace quantities of oxygen upon the thermal decomposition of hydrocarbons is being examined. A continuous flow reactor is employed, with reaction times on the order of 0.1-0.3 seconds. Initial oxygen concentrations vary from 1% down to 0.001%. Oxygen is found to increase the rate of decomposition even when present in low concentration. Particular attention is paid to the effect of the oxygen on the reaction rate and the decomposition yield spectrum; in this way it is possible to determine the mode of attack of oxygen on the hydrocarbon and to deduce the mechanism of the oxygen initiated decomposition.

5A76

LAWRENCE RADIATION LABORATORY-BERKELEY Chemistry Division

C. J. King 3/10/64

GAS LIQUID MASS TRANSFER

1. UNDER CONDITIONS OF EXTREME AGITATION

Rates of gas absorption are being measured in a continuous flow, rapidly stirred vessel. Several sparingly soluble gases are employed to determine the effect of solute diffusivity on the liquid phase mass transfer coefficient. The results will indicate whether or not the process can become turbulence-controlled under very high rates of agitation, and will test the surface-renewal theories of mass transfer. The study will also ascertain whether there is an upper limit to the absorption rate per unit volume in an agitated two phase fluid medium.

2. ADDITIVITY OF INDIVIDUAL PHASE RESISTANCES

Theoretical studies are being carried out to assess the classical concept of the addition of individual phase coefficients in the design of mass transfer equipment. Among the significant effects uncovered and explored are (1) the interaction of individual phase coefficients and (2) the distribution of surface lifetimes within equipment. These factors are capable of resolving seeming anomalies in past data and provide guideposts for improved design techniques.

Computer solutions have been employed to predict the interaction effect in a simple, countercurrent contacting of two fluids. The rate of mass transfer is found to be significantly higher than the rate suggested by the addition of resistances concept.

5A77

LAWRENCE RADIATION LABORATORY - BERKELEY   Chemistry Division

Warren M. Garrison   3/10/64

BASIC MECHANISMS IN THE RADIOLYSIS OF AMINO ACIDS, PEPTIDES AND RELATED COMPOUNDS

Studies include quantitative determination of reaction products and stoichiometries and identification of the intermediate processes by which the energy of excitation and ionization absorbed in the primary act is manifested as chemical change. Both aqueous and solid-state systems are involved. We find, for example, that the radiation chemistry of the simple α-amino acids in oxygen-free solution is initiated by the reactions (i) $e^-_{aq} + NH_3^+CH(R)COO^- \rightarrow NH_3 + CH(R)COO^-$ (ii) $H + NH_3^+CH(R)COO^- \rightarrow H_2 + NH_3^+\dot{C}(R)COO^-$ (iii) $OH + NH_3^+CHRCOO^- \rightarrow H_2O + NH_3^+\dot{C}(R)COO^-$. Effects of side-chain substitution on the above elementary reactions and on competing reactions involving side-chain loci are being measured. Peptides in aqueous solution undergo OH attack similar to that observed with amino acids. In oxygenated solutions the peptide radical is removed in the schematic step $\sim CONH\text{-}\dot{C}(R) + O_2 \rightarrow \sim CON{=}C(R) + HO_2$. Mild hydrolysis of the dehydropeptide (or its hydrate) yields ammonia and α-keto acid. This reaction is being used to study the effects of amino acid composition and molecular configuration on the rate and locus of reactions of protein and synthetic polypeptides with the OH radical.

Many of the intermediates formed in aqueous solution are also produced in solid-state system. The radiation-induced coloration of proteins has recently been shown to be related to the formation of dehydropeptide linkages at aromatic amino-acid sites. However, long-lived peptide radicals ($\sim CON\text{-}\dot{C}(R)\sim$) represent the major degradation products in the radiolysis of protein and polypeptide in vacuo. The combined yield of peptide radicals formed in the γ-radiolysis of a variety of proteins and polypeptides i.e. $G(NH_3)$ is in the range 2 to 4. Studies of gaseous products under identical conditions give $G(H_2) \leq 0.3$. Present evidence is that the reaction $\sim CONH\text{-}CH(R)\sim \rightsquigarrow H + \sim CONH\text{-}\dot{C}(R)\sim$ does not represent a major path for formation of peptide radicals. Studies of gaseous products are being made with finely divided fibrils. When proteins and synthetic polypeptides in this form are irradiated under oxygen, the observed yields of both ammonia and carbonyl are increased by an order of magnitude. Oxygen is apparently reacting with states that are chemically ineffective in vacuo.

SECTION 5B

LAWRENCE RADIATION LABORATORY - BERKELEY
INORGANIC MATERIALS RESEARCH DIVISION

5B1 Metal Phase Diagrams

5B2 Thermodynamic Compilations

5B3 Radiative Lifetimes of Excited Electronic States

5B4 New Spectral Methods

5B5 Absorption Coefficients of High Temperature Molecules

5B6 Kinetic and Stoichiometric Studies of Hydrated Metal Ions

5B7 The Chemistry of Sulfur-Nitrogen Compounds

5B8 The Chemistry of Hydrides

5B9 Liquid Ammonia Chemistry

5B10 Ultra-High Pressure Research: Thermodynamics of Metals Under Pressure

5B11 Ultra-High Pressure Research: Resistance Measurements

5B12 Ultra-High Pressure Research: Heat Conductivity of Insulators Under Pressure

5B13 Ultra-High Pressure Research: Mössbauer Measurements Under Pressure

5B14 Nature of Ionized Gases

5B15 Photosensitized Ionization

5B16 Kinetics of Electron Reactions

5B17 Reaction Kinetics by Paramagnetic Resonance

5B18 The Kinetics of Chlorination of UCl_4 In A Fused Salt

5B19 Kinetics of Liquid-Metal Extraction

5B20 Diffusion-Controlled Oxidation of the Refractory Metals

5B21 The Graphite-Hydrogen System

5B22 Elastic Scattering of Crossed Alkali Metal Beams

5B23 Chemical Reactions Induced by Fission Fragment Irradiation

5B24 Low Temperature Calorimetry

5B25 Studies of Molecular Structure Using NMR Techniques

5B26 New Methods for Following and Characterizing Gas-Phase Species at Very Low Concentrations

5B27 Electrode-Electrolyte Reactions

5B28 Electrochemistry

5B29 Transport of Charge and Mass in Electrochemical Systems

5B30 Nonaqueous Ionizing Solvent Media, and Uncommon Electrode Reactions

For further information on completed work, the reader is referred to the open scientific literature and to the Lawrence Radiation Laboratory, Berkeley, Inorganic Materials Research Division Annual Report for the year ending December 31, 1962, Report Number UCRL 10706.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Leo Brewer

2/10/64

METAL PHASE DIAGRAMS

A preliminary evaluation of the fundamental electronic factors which can be correlated with thermodynamic stability of metal phases has been published. The Engel theory of metals was used to relate the structures and stability of metallic phases through the use of bonding concepts that are successful in describing the chemical behavior of conventional materials. The structures of the possible phases and their maximum composition ranges have been described in text, tables, and in the form of multicomponent phase diagrams for the various combinations of thirty transition metals. These diagrams are being used to guide choices of compositions for superconductivity studies.

Publications

1. L. Brewer, "Thermodynamic Stability and Bond Character in Relation to Electronic Structure and Crystal Structure," paper in Electronic Structure and Alloy Chemistry of the Transition Elements, Ed. Paul A. Beck, Interscience, New York, 1963.

2. L. Brewer, "Prediction of High Temperature Metallic Phase Diagrams," UCRL-10701, July, 1963.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Leo Brewer

2/11/64

THERMODYNAMIC COMPILATIONS

Methods have been developed for the prediction of low-lying electronic states of gaseous diatomic and triatomic molecules and have been used to assist in the critical evaluation and compilation of thermodynamic data for the gaseous metal dioxides and dihalides. A similar critical evaluation of high temperature vaporization data and consistent estimation of partition functions is underway for the gaseous metal monoxides. The application of these data to high temperature purification procedures has been illustrated for removal of oxygen from metals. It is planned to illustrate the use of such thermodynamic data in the design of the high temperature purification processes for removal of iron from refractory metals.

The available data for nitrides, carbides, sulfides, and halides of molybdenum have been critically evaluated and estimated values tabulated when no data were available. During the next two years, it is planned to consolidate these previous compilations which are over 10 years old, to bring them up to date, and to compile complete thermodynamic tables for Mo and its compounds.

Publications

1. L. Brewer and G. M. Rosenblatt, "Dissociation Energies of Gaseous Metal Dioxides," Chem. Rev., 61, 257(1961).

2. L. Brewer, G. R. Somayajulu, and E. Brackett, "Thermodynamic Properties of Gaseous Metal Dihalides," Chem. Rev., 63, 111 (1963).

3. L. Brewer and G. M. Rosenblatt, Trans AIME, 224, 1268(1962).

5B3

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Leo Brewer/J. Link/A. Chutjian/R. Walsh

2/11/64

RADIATIVE LIFETIMES OF EXCITED ELECTRONIC STATES

An apparatus for measurement of radiative lifetimes in the range of 10^{-5} to 10^{-9} seconds has been applied to fluorescent solids, organic compounds, and to the $v' = 26$ level of the $B^3\Pi$ state of gaseous iodine. Its use has now been extended to gaseous sodium and other atoms and additional organic compounds. Further work is underway using various atomic light sources to excite different rotational and vibrational levels of the $^3\Pi$ state of I_2 to determine the variation of lifetime with rotational and vibration excitation and to measure the lifetimes of various electronic states of the alkali metals.

Gaseous I_2 has been successfully studied in a molecular beam and the method is being extended to molecular beams of the high temperature molecules LaO and CN.

Publications

1. S. J. Strickler and R. A. Berg, "Relationship between Absorption Intensity and Fluorescence Lifetime of Molecules," J. Chem. Phys., 37, 814 (1962).

2. L. Brewer, R. A. Berg, G. M. Rosenblatt, "Radiative Lifetimes of I_2 Fluorescence, $B^3\Pi_{0^+\mu} - X'\Sigma_{0^+g}$", J. Chem. Phys. 38, 1381 (1963).

5B4

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Leo Brewer/B. Meyer/R. Walsh/R. Hauge

2/11/64

NEW SPECTRAL METHODS

An attempt will be made to develop new methods of analyzing electronic spectra. Absorption spectra of high temperature molecular beams have been obtained in an effort to establish the ground states. The polarization of fluorescence for molecular beams will be examined in an effort to detect Q branches and heads. The possibility of electronic Raman spectra of molecular beams is being considered.

It has been found that sharp electronic spectra of high temperature atoms and molecules trapped in rare gas matrixes at liquid helium and hydrogen temperatures can be obtained. Forbidden transitions such as the infra-red vibration spectrum of S_2 can be seen in matrixes. The spectra of a variety of high temperature molecules in rare gas as well as polar matrices are being studied.

Publication

1. B. Meyer, "Vibration Spectrum of Trapped S_2", J. Chem. Phys. 37, 1577(1962).

5B5

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Leo Brewer/M. Shetlar/R. Hauge/R. Walsh

2/11/64

ABSORPTION COEFFICIENTS OF HIGH TEMPERATURE MOLECULES

Measurements of absolute absorption and emission intensities of C_2 and CN spectral features in the King furnace have been combined with estimates of equilibrium partial pressures in the King furnace to calculate radiative lifetimes. When directly measured radiative lifetimes become available for these molecules, the calculations can then be reversed to obtain accurate values of the equilibrium concentrations and free energies and enthalpies of formation of C_2 and CN. Similar work is planned for LaO, Si_2, and MgCl.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

R. E. Connick

2/10/64

KINETIC AND STOICHIOMETRIC STUDIES OF HYDRATED METAL IONS

The observation of the broadening of the O^{17} NMR resonance of water has permitted measurement of very rapid rates of water exchange in and out of the first coordination sphere of a number of paramagnetic ions. This type of measurement will be extended to other magnetic cations and the temperature range covered by the original measurements will be broadened to yield additional information on exchange kinetics and the relaxation process. An extensive set of data should reveal the primary factors controlling these rates of exchange. The change in the water exchange rate brought about by complexing of the metal ion by ligands other than water is also being investigated.

Work has started on measuring the number of water molecules in the first coordination sphere of diamagnetic cations whose exchange is sufficiently slow to yield a separate O^{17} resonance for the bound water. In certain cases it will be possible to obtain rates of exchange from temperature dependence studies.

Time permitting, determinations of oxygen bridging in hydrolyzed cationic polymers and poly acids will be attempted using the O^{17} NMR resonance.

Publication

1. Swift and Connick, "NMR-Relaxation Mechanisms of O^{17} in Aqueous Solutions of Paramagnetic Cations and the Lifetime of Water Molecules in the First Coordination Sphere," J. Chem. Phys., 37, 307 (1962).

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

William L. Jolly

2/10/64

THE CHEMISTRY OF SULFUR-NITROGEN COMPOUNDS

The chemistry of compounds containing sulfur-nitrogen bonds represents a large, although little understood, branch of inorganic chemistry. We are attempting to systematize the reactions of these compounds.

Recently we reported four new methods for preparing NSCl and new, improved methods for the preparation of $S_3N_2Cl_2$, S_3N_2Cl, $S_3N_3Cl_3$ and S_4N_3Cl. As an off-shoot of these studies, we are presently investigating the nature of the reaction of HCl with S_4N_4. The reaction of ammonia with S_2Cl_2 to produce, among other things, S_4N_4, S_7NH, and S_8 is being studied to determine the optimum conditions for the preparation of S_4N_4 and S_7NH. It appears that various sulfur-nitrogen-chlorine compounds are formed as intermediates in this reaction, and perhaps some of these can be isolated.

We have found that solutions of S_4N_4 in tetrahydrofuran can be titrated with solutions of sodium naphthaleneide to form a series of species, probably of the type $S_4N_4^-$, $S_4N_4^{2-}$, etc. We plan to follow the course of the reaction by measuring the u.v. absorption spectra and e.s.r. spectra of the solutions. Other species, such as the $S_4N_3^+$ ion, will also be titrated.

The reactions of atomic nitrogen with a variety of sulfur-containing compounds are being systematically studied. So far we have found that sulfur vapor reacts to give S_4N_2, that S_2Cl_2 reacts to give NSCl, and that H_2S reacts to give S_4N_4.

Publications

1. Jolly, Maguire, and Rabinovich, "Convenient Methods for Preparing $S_3N_2Cl_2$ and S_4N_3Cl," Inorg. Chem. 2 1304 (1963).

2. Jolly, Maguire and Smith, "Four New Methods for Preparing NSCl," Chem. and Ind., 1589, (1963).

LAWRENCE RADIATION LABORATORY - BERKELEY
Inorganic Materials
Research Division

William L. Jolly

2/10/64

THE CHEMISTRY OF HYDRIDES

We have found that it is possible to prepare the higher hydrides of silicon and germanium, as well as their phosphorus- and arsenic substituted derivatives, by the action of a silent electric discharge on the simple hydrides. It will be interesting to compare these new compounds with the structurally analogous hydrocarbons, organo-phosphines, and organo-arsines in order to determine which properties are similar and which are markedly different.

We are currently studying the n.m.r. and infrared spectra of trisilane and both isomers of tetrasilane. We are now engaged in preparing the isomers $SiH_3SiH_2PH_2$ and SiH_3PHSiH_3 in large enough quantities to permit the measurement of their physical and chemical properties. By studying the effect of the electric discharge on mixtures of SiH_4 and SiH_3PH_2, and of Si_2H_6 and PH_3, we hope to get an insight to the mechanism of the discharge tube reaction.

We plan to study the reactivity of species such as germane and digermane with the borohydride ion. Preliminary data suggest that it is possible to prepare the ion GeH_3BH_3.

Practically nothing is known of the mechanism whereby the borohydride ion reduces inorganic species in aqueous solution. As a start toward obtaining this information, we are studying the kinetics of the reduction of ferricyanide to ferrocyanide.

Publication

1. Jolly, "Hydrides of Germanium, Tin, Arsenic and Antimony," Inorg. Synthesis, 1, 34 (1963).

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

William L. Jolly

2/10/64

LIQUID AMMONIA CHEMISTRY

We have recently completed studies of the absorption spectrum of calcium in liquid ammonia and the calcium-ammonia phase diagram. Projected studies in liquid ammonia chemistry include:

(1) A study of the kinetics of the reactions of the electron with various species such as NH_4^+, ROH, NO_2^-, MuO_4^-, etc. It will be interesting to compare the rate constants for these reactions with the rate constants for the corresponding reactions in aqueous solutions.

(2) A study of the rates of proton exchange reactions in liquid ammonia by means of n.m.r. measurements. Such rates are often acid- or base-catalyzed, so it may be possible to establish a relative acidity scale in liquid ammonia. This would be extremely useful in other physical chemical studies in this solvent.

(3) A direct measurement of the equilibrium constant of the reaction

$$NH_2^- + \tfrac{1}{2}H_2 = NH_3 + e^-.$$

Publication

1. Jolly and Hollada, "Absorption Spectra of Calcium-Ammonia Solutions," Inorg. Chem. 2, 1076 (1963).

5B10

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

George Jura

2/11/64

ULTRA-HIGH PRESSURE RESEARCH: THERMODYNAMICS OF METALS UNDER PRESSURE

One of the objectives of the high pressure program is the determination of the thermodynamic properties of materials under high pressures. Except for very special cases, namely hydrogen at helium temperatures, no direct measurement of a high pressure thermal property of any solid has been made. The difficulty in these measurements is that the heat capacity of the container is much larger than the heat capacity of the system under consideration. Also, the heat leak is very large. We believe that in the case of metals these difficulties can be solved through the measurement of electrical resistance.

Since the resistance of a metal can be determined as a function of the temperature, the temperature can be determined by a resistance measurement. If a pulse of electrical energy is passed through the sample, heating it, the energy in the pulse and the rise in resistance (temperature) can both be measured. If the pulse is of sufficiently short duration, and if the resistance measurement is made rapidly enough, then the average heat capacity between the original and final temperature may be determined. By using various starting temperatures, this data can be differentiated and the actual heat capacity determined as a function of the temperature and pressure of the sample. Calculations of the thermal conductivity of silver chloride show that in 2 microseconds less than 1% of the heat will be conducted away from the sample if the temperature rise of the sample is about 200°C. In order to raise the temperature of the sample this much, the pulse must have an energy of about 0.2 joules, delivered in less than one microsecond.

Resistance measurements in a short time period is not difficult. It is hoped that the electrical problems of switching and obtaining a sufficiently large pulse of energy in the necessary time will be solved during the next six months.

LAWRENCE RADIATION LABORATORY - BERKELEY
Inorganic Materials
Research Division

George Jura

2/11/64

ULTRA-HIGH PRESSURE RESEARCH: RESISTANCE MEASUREMENTS

Reliable resistance measurements can now be made with an accuracy of 0.01%. The major effort at the present time is directed toward an extension of the working temperature range from 77°K to about 600°K. In order to obtain higher temperatures it has been necessary to use more complex pressure devices than Bridgman anvils. By using resistive heating we have reached a temperature of at least 1400°K, with no damage to anvils.

The technique of internal heating is a definite asset in the study of phase transformation under pressure. Preliminary studies of iron and bismuth have been made. The iron transition has been difficult to study under nearly hydrostatic conditions, since the transformation would start sometimes at a pressure of 160 kbars and at other times at a pressure over 200 kbars although even when the transition has been as highly overdriven, the transition would still take about 50 kbars to be completed. Preliminary measurements using internal heating give a sharp transition at about 110 kbars.

The bismuth 6-8 transition has been surveyed. By judicious heating it has been possible to transform the material to the two-phase region, and watch one of the phases grow at the expense of the other.

With this technique, the preliminary value for this transition is 80 kbars, as compared to the previously determined 88 kbars.

LAWRENCE RADIATION LABORATORY - BERKELEY
Inorganic Materials
Research Division

George Jura

2/11/64

ULTRA-HIGH PRESSURE RESEARCH: HEAT CONDUCTIVITY OF INSULATORS UNDER PRESSURE

This measurement is a byproduct of our early attempts to determine the heat capacities of metals. We have found that after heavily pulsing a metal sample, and then following the resistance as a function of time, the temperature decay is controlled by the temperature of the medium rather than that of the sample. By placing probes at various positions with respect to the sample, it is possible to determine the temperature gradient in the insulator. By measuring the energy input in a steady state, it becomes possible to determine the flow of heat through the insulating material. If these measurements could be carried out over a sufficiently wide range of temperatures, it would become possible to approximate, among other quantities, the Debye temperature of the insulator.

5B13

LAWRENCE RADIATION LABORATORY - BERKELEY
Inorganic Materials
Research Division

George Jura

2/11/64

ULTRA-HIGH PRESSURE RESEARCH: MOSSBAUER MEASUREMENTS UNDER PRESSURE

Determinations of the Mossbauer effect under pressure with Dy^{161} and Fe^{57} show the importance of this technique in high pressure studies. In the case of iron, the experiments became impossible when the data became the most interesting; when the iron started to transform to the high pressure phase. The first experiments did not permit us to conclude studies of the magnetic nature of the high pressure phase.

Studies of the geometry and containing rings are under progress. These studies will enable us to make determinations at higher pressures. Other physical methods, namely heating, will enable us to determine the spectrum of iron after it has been completely transformed to the high pressure phase. This in turn will enable us to determine the magnetic properties of the high pressure form. There also will be an attempt to make these determinations as a function of temperatures as well as pressure. In general when a Mossbauer nucleus is available, it will be posssible in many cases to determine the magnetic properties of the material under study as a function of interatomic distance. These results could be important in the understanding of the ferromagnetic state.

In the Dy^{161} work, we found that under certain circumstances placing the sample under pressure induced the formation of a high resolution spectrum. The development of a hyperfine structure, and the increase in the separation of lines with pressure developed an increasingly complex fine structure to a pressure of 50 kbars. Above this pressure no further resolution of the spectrum occurred. It is our belief that it was the absorber that was limiting the resolution. We are now building a system whereby the absorber can be maintained at any temperature down to helium temperatures. This system which will be of value for many systems, will be tested with a solution of gold in iron.

Publication

1. Jura and Nicol, "The Effect of Pressure on the Mossbauer Spectrum of Fe^{57} in Iron Metal," Science, 141, 3585, 1035-38 (1963).

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

B. H. Mahan

2/10/64

NATURE OF IONIZED GASES

The rates of mutual charge neutralization of gaseous ions have been investigated. For example, the rate constants for the following processes have been determined:

$$NO^{+} + NO_2^{-} \xrightarrow{k_o} \text{neutrals}$$

$$NO^{+} + NO_2^{-} \xrightarrow{k_1} (NO^{+}NO_2^{-})^{*}$$

$$(NO^{+}NO_2^{-})^{*} \xrightarrow{k_2} NO^{+} \quad NO_2^{-}$$

$$(NO^{+}NO_2^{-})^{*} + M \xrightarrow{k_3} (NO^{+}NO_2^{-}) + M \longrightarrow \text{neutrals}$$

Here, $(NO^{+}NO_2^{-})^{*}$ is a pair of ions close to each other, but with enough energy to separate, $(NO^{+}NO_2^{-})$ is a pair of ions that are bound to each other, and M is a molecule of a neutral inert gas. In order to understand the magnitudes of these rate constants, it is important to know what fraction of the ions are tied up in complexes with the inert neutral molecules. That is, we must know the value of the equilibrium constant for

$$NO^{+} + Ar = NO^{+}Ar$$

and other similar reactions. We have begun the construction of a mass spectrometer which will examine these ionized gases and which will be used to determine equilibrium constants as a function of temperature. This investigation will give us information about the magnitudes of ion-neutral binding energies, as well as the data necessary to understand ion neutralization rates.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

B. H. Mahan

2/10/64

PHOTOSENSITIZED IONIZATION

The ionization resulting from the reactions of electronically excited atoms is being studied. At present, we are trying to find the threshold frequency for the reaction

$$Cs + h\nu \rightarrow Cs^* \qquad (1)$$

$$Cs^* + Cs \rightarrow Cs_2^+ + e \qquad (2)$$

The difference between the threshold energy for this ionization process and for the direct photoionization of the cesium atom

$$Cs + h\nu \rightarrow Cs^+ + e \qquad (3)$$

is a lower limit for the bond energy in CS_2. This type of measurement will be extended to the other alkali metals to determine the bond energies in Na_2, K_2, and Rb_2. These bond energies are of fundamental interest, since the one electron bonds are the simplest possible.

The second part of this problem is to determine the rates of processes represented by reaction (2). The electronic state represented by Cs^* will be known, and the whole system can be described in terms of rather simple wave functions. Thus it may be possible to make a meaningful comparison between experimental and calculated reaction cross sections.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

B. H. Mahan

2/10/64

KINETICS OF ELECTRON REACTIONS

By using microwave cavity resonance techniques, it is possible to measure the concentration of gaseous thermal electrons. This method can be used to study the kinetics of the elementary reactions of electrons. For example,

$$e + NO_2 + Ar \rightarrow NO_2^- + Ar \qquad (1)$$

$$e + N_2O \rightarrow N_2 + O^- \qquad (2)$$

$$e + NO^+ \rightarrow N + O \qquad (3)$$

are three different types of reactions that gaseous electrons undergo. Reaction (1) is presently under investigation. It is of practical interest because NO_2^- is an important negative ion in the upper atmosphere. The theoretical analysis of such a reaction in which the de Broglie wave length of the electron is large compared to the extent of the fields of the molecules is possible, and indicates that the data can be analyzed to give a limit for the lifetime of the electron on NO_2 in the process.

$$e + NO_2 \rightarrow (NO_2^-)^*$$

$$(NO_2^-)^* \rightarrow NO_2 + e$$

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

B. H. Mahan/R. Myers

2/10/64

REACTION KINETICS BY PARAMAGNETIC RESONANCE

Electron paramagnetic resonance permits the direct observation of gaseous free radicals, and can be used to study the rates of their chemical reactions. There are no completely satisfactory measurements of the rates of

$$O + O + Ar \rightarrow O_2 + Ar$$

$$N + N + Ar \rightarrow N_2 + Ar$$

$$H + H + Ar \rightarrow H_2 + Ar$$

and we intend to determine the rate constants for these reactions within the next year. They are of particular interest because the potential energy surfaces are well known, and the rate data can be interpreted theoretically.

As a second part of the program, metathetical free radical reactions will be studied. For example,

$$H + O_2 \rightarrow OH + O$$

$$O + H_2 \rightarrow OH + H$$

are reactions in which both product and reactant radicals can be detected. This allows a more certain determination of reaction mechanisms and rate constants in these potentially more complicated systems to be made, and in some cases gives rate information that cannot be obtained by any other technique.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Donald R. Olander

2/10/64

THE KINETICS OF CHLORINATION OF UCl_4 IN A FUSED SALT

This program is concerned with investigating the kinetics of the reaction: $UCl_4(\ell) + Cl_2(g) \rightarrow UCl_6(g)$, which occurs at the interface between a fused UCl_4-LiCl-KCl salt mixture and an atmosphere of chlorine gas. The process involves diffusional transport of the reactants to the phase boundary, chemical conversion at the interface, and removal of the reaction products to the bulk phases. The overall rate depends upon the relative magnitudes of the diffusion and chemical reaction steps.

In order to permit direct calculation of the mass transfer contribution from experimental data, a laminar jet contacting device is employed. The nickel reaction vessel is approximately 10" high and 4" in diameter. It is divided into two sections by a nickel plate which is pierced by a 1 mm orifice. The molten salt (containing UCl_4) is fed to the upper section from a feed tank and is maintained at a constant level by a level controller. The jet exiting from the orifice leaves the reaction section via a 2 mm capillary, and is collected in a receiving tank.

Preheated chlorine gas is fed to the bottom section of the vessel and removed (along with any UCl_6 formed) at the middle. The exit gas is then analyzed for UCl_6. In order to ascertain that the jet is operating properly and not spilling over the capillary, a quartz window and a mirror are provided for direct observation. The entire vessel is placed in a resistance furnace which provides temperatures of 400-600°C.

A theoretical investigation of diffusion limited surface reactions in this system, based upon boundary layer approximations to the gas phase hydrodynamics, is also being conducted.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Donald R. Olander

2/10/64

KINETICS OF LIQUID-METAL EXTRACTION

This study is concerned with the kinetics of extraction of a solute metal between two liquid-metal solvents. Radioactive cerium metal is to be extracted from a molten uranium-chromium eutectic drop as it falls through liquid magnesium.

The extraction kinetics will be studied in a 2" diameter, 4' high tantalum tube containing 2 kg of molten magnesium metal at 860-900°C. The magnesium metal floats on a layer of fused sodium chloride-potassium chloride-mixed salt. A solid pellet of the uranium-chromium eutectic ~1 mm in diameter is dropped into the top of the column, melted in the magnesium layer and resolidified as it passes through the salt layer, which is held below the melting point of the drop material. Each small droplet contain ~1 mc of total activity, obtained by irradiation in the Livermore reactor. This radioactivity enables radiation detectors to follow the progress of the drop down the column, and permits rapid analysis of the cerium content before and after extraction. The solidified drop is removed from the column by valves and falls into a container which is held in a lead cask. Similar drop extractors have been used for pyrometallurgical studies at the Brookhaven National Laboratory.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Donald R. Olander

2/10/64

DIFFUSION-CONTROLLED OXIDATION OF THE REFRACTORY METALS

The oxides of the refractory metals molybdenum, tungsten, tantalum, and niobium melt or sublime at temperatures considerably lower than the melting point of the parent metal. The absence of a protective oxide coating in high temperature oxidizing atmospheres implies that the rate of oxidation will be controlled either by the chemical kinetics of the surface reaction or by the diffusional resistance to oxygen transport to the surface or metal oxide removal from the surface; the importance of both of these steps has been demonstrated in the case of molybdenum.

The kinetics of the oxidation of these refractory metals will be studied at temperatures in the neighborhood of the sublimation point of the principal oxide in a device which permits accurate estimation of the diffusional resistance.

The material to be studied initially is molybdenum; its volatile oxide (MoO_3) sublimes at 1150°C, nearly 1500°C below the melting point of the metal. The flow system to be used is the rotating disk, for which the combined momentum, energy and diffusion equations are amenable to exact numerical solution. Since at the temperatures of interest, both chemical reactions and diffusion offer important resistance to oxidation, a system of predictable hydrodynamic and diffusional properties is necessary for the evaluation of the chemical rate constant from the overall kinetic data.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Donald R. Olander

2/10/64

THE GRAPHITE-HYDROGEN SYSTEM

The primary heterogeneous reactions between molecular hydrogen and graphite are to be studied by a modulated molecular beam technique similar to that developed by Fite.

A molecular beam of hydrogen effuses from an oven source at a prescribed temperature through a collimating slit into the main reaction chamber, maintained at 10^{-5} mm Hg, and where it impinges upon a heated graphite surface. A small fraction of the hydrocarbon reaction products (CH, CH_2, CH_3, and higher hydrocarbons) enter the ionization chamber of a mass spectrometer, and the resulting ion currents are mass-analyzed and measured by an electron multiplier.

A signal to noise ratio sufficient to identify primary reaction products can be obtained by modulating the primary hydrogen and detecting only the AC component of the predominantly DC ion current.

The primary objective of the work is to identify the carbon containing species resulting from the surface reactions. The probability of hydrogen reacting to form each of the hydrocarbons will be measured as a function of temperature. Future work will involve reaction of the graphite by atomic hydrogen. The effect of ionization radiation upon the graphite will also be studied.

LAWRENCE RADIATION LABORATORY - BERKELEY
Inorganic Materials
Research Division

Donald R. Olander
2/10/64

ELASTIC SCATTERING OF CROSSED ALKALI METAL BEAMS

The differential elastic scattering cross sections of the alkali metals are to be measured by scattering of crossed atomic beams. From these measurements, the interatomic potentials can be obtained by the usual kinetic theory methods. In addition, the transport properties of the gas phase can be computed directly from the differential cross sections.

The experimental set up will be similar to that employed by Beck. Two beams of alkali metals (e.g., K-K) will be crossed in a chamber held at $\sim 10^{-5}$ mm Hg. The beams will be velocity-selected to provide nearly mono-energetic collisions. The oven and velocity selection chambers will be separated from the main scattering chamber by partitions which contain small collimating slits. Each of the chambers will be differentially pumped, and the main chamber cooled by liquid nitrogen in the region of impingement of the main beams. The relative velocity will be adjusted either by altering the source oven temperatures or by varying the angle of intersection of the two beams. The angular distribution of the scattering particles will be measured by a movable surface ionization gauge of suitably high angular resolution.

LAWRENCE RADIATION LABORATORY - BERKELEY
Inorganic Materials
Research Division

Donald E. Olander

2/10/64

CHEMICAL REACTIONS INDUCED BY FISSION FRAGMENT IRRADIATION

The objective of this program is to measure the build-up of stable products and unstable intermediates in the radiation-induced conversion of ammonia to hydrazine. This system has been chosen because of the relatively small number of species expected (i.e., H_2, N_2, NH_3 and N_2H_4) and the free radicals H, N and NH_2.

Mass spectrometric methods similar to those employed to follow reactions in cool flames will be used for analysis of the mixture during irradiation. The irradiation chamber will be pierced by a small orifice through which a representative sample of the gas effuses to the ionizing chamber of the mass spectrometer. In order to prevent further reaction between the sampling orifice and the ionizer, either by collisions in the gas phase or with the container, the flow through the orifice must be molecular. At the low pressures required, a highly ionizing form of radiation must be used to deposit a sufficient amount of energy in the reaction mixture. Fission fragment radiation will be employed. The inner walls of the reaction chamber will be coated with finely divided particles ($\sim$2-3μ diameter) of enriched UO_2; the chamber will be exposed to a neutron flux. Under steady state operation, the approach to radiation equilibrium will be followed.

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

N. E. Phillips

2/10/64

LOW TEMPERATURE CALORIMETRY

Experimental work is concerned with the interval between 0.07°K and 20°K with the emphasis on the relatively unexplored regions below 1°K and from 4 to 15°K. The calorimeters used are of two distinct types. The first employs the technique of adiabatic demagnetization to cover the region from 1°K to the lowest temperatures. Experiments are in progress to improve the accuracy of temperature measurements below 0.1°K and to extend the measurements to lower temperatures. The second type of calorimeter employs liquid H_2 and liquid He^4 to produce temperatures between 1°K and 20°K, and in some cases a He^3 stage is added to extend the range to 0.3°K. A special apparatus for the calibration of germanium thermometers between 0.3°K and 20°K is being made.

Measurements in progress or planned for the next year include the following:

1) Magnetic hyperfine heat capacities in ferromagnetic and antiferromagnetic metals. In some cases it should be possible to determine the sign of the hyperfine field by making measurements in a magnetic field.

2) The heat capacity of solid rare gases at pressures up to 10,000 atmosphere.

3) Spin wave heat capacities of ferromagnets and antiferromagnets.

4) Comparison of elastic constants and lattice heat capacity in superconducting and normal metals.

Publications

1. Phillips, Ho and O'Neal, "Low Temperature Heat Capacities of Constantin and Manganin," Rev. Sci. Inst. 34 7, 782-83(1963).

2. Ahlers, "Heat Capacity of Solid He^4 at the Density of the Gamma Phase," Phys. Rev. Letters, 10 439 (1963).

LAWRENCE RADIATION LABORATORY - BERKELEY
Inorganic Materials
Research Division

Charles H. Sederholm

2/10/64

STUDIES OF MOLECULAR STRUCTURE USING NMR TECHNIQUES

High resolution NMR techniques are being used to study the structure of molecules. In addition, correlations are being found between the structure of molecules and their NMR spectra.

A thorough study of the factors influencing fluorine-fluorine coupling constants has led to the conclusion that the direct overlap of nonbonding electrons around the two nuclei being coupled is as important to fluorine-fluorine coupling constants as are the bonding electrons in the molecule. The spin information carried by the bonding electrons is reduced as the electronegativity of the other atoms attached to the molecule is increased.

Measurements of fluorine NMR spectra over a wide temperature range have resulted in two types of information. Barriers to internal rotation in several halogen substituted ethanes containing at least one fluorine atom have been determined and some correlation has been established between the barrier heights and the size of the halogen substitutents. The time weighted average approximation for chemical shifts and coupling constants has been tested in several compounds and it has been demonstrated that solvent effects can cause serious exceptions to this approximation. The effect solvents have on coupling constants is being further investigated.

Proton geminal coupling constants are predicted to vary with the H-C-H bond angle. For a normal tetrahedral angle the coupling constant is predicted to be and is generally found to be roughly 8-12 cps. In several four membered ring compounds the geminal coupling constant has turned out to be quite small; on the order of 2-3 cps. Geminal coupling constants in four membered rings are being further investigated to determine which factors affect their size.

5B26

LAWRENCE RADIATION LABORATORY - BERKELEY
Inorganic Materials
Research Division

Harold S. Johnston
2/7/64

NEW METHODS FOR FOLLOWING AND CHARACTERIZING GAS-PHASE SPECIES AT VERY LOW CONCENTRATIONS

Mechanisms of gas-phase chemical reactions typically involve many elementary reactions, in series and in parallel, and to explain experimental results one usually must postulate one or more free radicals, free atoms, excited electronic states, or other reactive intermediates. By means of flash photolysis, shock tubes, high intensity pulses of beam sources, etc., one can sometimes obtain observable concentrations of reactive intermediates. On the other hand it is highly desirable to develop methods of very high sensitivity, and that is the object of this work.

One method being developed is fairly standard; it uses modulated photochemical excitation and a phase sensitive detector. The method of greatest interest is to use the decay constant of light in an optical cavity to measure light absorption. With modern multi-layer dielectric coatings and moderate cell lengths (3 meters), this method gives promise for measuring species at particle densities of 10^{12+2} per cc. The method demands a high speed Kerr cell and electronic counting in the nanosecond time range.

5B27

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

R. H. Muller

3/1/64

ELECTRODE-ELECTROLYTE REACTIONS

Studies will be conducted on the preparation and characterization of solid-fluid interfaces. Of special interest are the properties of electrolytically prepared metal surfaces and the influence of adsorbed or reacted interfacial layers on kinetic parameters. Ellipsometry, which is sensitive to transitional layers of atomic dimensions, promises to be a powerful tool for this work. Later studies will include the electrolytic crystal growth on surfaces of defined characteristics, preferably single crystal faces. Optical electron and field ion microscopy are being considered as experimental techniques in this phase.

Electrolyte films on gas consuming electrodes will be investigated in detail and theoretical reasons for the observed phenomena will be sought. Refraction and adsorption indices for light reflected at the solid-liquid interface will be measured with an ellipsometer to determine the exact value of the optical phase retardation. Knowledge of these quantities is needed to ascertain the position of the zero point in film thickness measurements.

Efforts to measure current distributions in pore models of realistic critical dimension will be continued. In a new high precision assembly under construction, the width of each electrode section is being decreased to provide a better resolution of current distribution. At the same time, the width of the separating insulation between sections is being decreased and its construction revised so as to reduce dead surface and chance of cold flow.

LAWRENCE RADIATION LABORATORY - BERKELEY
Inorganic Materials
Research Division

E. Grens

2/13/64

ELECTROCHEMISTRY

Experimental studies of current distribution in electrodes with fissure-type pores are being carried out. This work involves measurement of a redox reaction as a function of depth in a single fissure (of micron order width) which serves as one electrode of a laboratory cell.

The rates of dissolution of porous metal anodes undergoing electrolysis are being measured. The dependence of these rates upon position and pore depth in the electrodes is of concern in the work being performed.

Investigation of the initiation and course of the reaction of liquid droplets (or solid particles) suspended in gaseous atmosphere containing both inert and reactive components is planned. The effects of the composition and temperature of the gaseous atmosphere upon the course of the reactions that may occur are to be investigated.

Measurements of transport parameters for systems with simultaneous heat and mass transfer, in particular thermocells, are to be made, and interpretation of experimental data by methods of nonequilibrium thermodynamics will be made.

5B29

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Charles W. Tobias

2/10/64

TRANSPORT OF CHARGE AND MASS IN ELECTROCHEMICAL SYSTEMS

Both experimental and theoretical studies are being carried out to permit improved description and understanding of transport phenomena in electrochemical systems. Development of precise numerical techniques for the evaluation of current distribution in two-dimensional enclosures is underway. Experimental studies of current distribution, and the variation of rates of dissolution throughout a porous metal electrode are being studied.* Studies of transport properties in concentrated electrolytes are being made.** Finally, studies of the effect of mass transport on current distribution on "rough" surfaces are being carried out.

*Partially supported by NASA Research Grant NsG 150-61.
**Partially supported by Contract No. DA36-039-SC-89153.

5B30

LAWRENCE RADIATION LABORATORY - BERKELEY

Inorganic Materials
Research Division

Charles W. Tobias

2/10/64

NONAQUEOUS IONIZING SOLVENT MEDIA, AND UNCOMMON ELECTRODE REACTIONS

Several different studies are being carried out on the electrochemistry of nonaqueous or unusual systems. Studies of the anodic oxidation of liquid phosphorus in aqueous media are being made. The physical properties and the electrochemical behavior of metallic solutions of calcium in liquid ammonia are being determined. The nature of the electromotive series in dimethyl sulfoxide is being explored.*** Lastly the mechanism of electrodes of the second kind in nonaqueous solvents is being examined.

***Partially supported by Contract No. N123(62738)23531A.

SECTION 6

NATIONAL BUREAU OF STANDARDS

6-1 Interactions at Gas-Solid Interfaces

6-2 Radiolysis of Organic and Inorganic Compounds

6-3 Vacuum Ultraviolet Photochemistry

6-4 Photoionization Studies

6-5 Flash Spectroscopy

6-6 Data of State for Gaseous Fluorides

6-7 Molecular Theory of Time - Dependent Phenomena

6-8 Infrared Spectra and Molecular Constants of Deuterated Molecules

6-9 Electrochemical Calorimetry

6-10 Calorimetric Determination of the Composition and of the Equilibrium Constant of Complexes Existing in Fused Salts

6-11 Collection, Analysis, and Compilation of Chemical Thermodynamic Data

For further information on completed work the reader is referred to the open scientific literature and to the publication "Research Highlights of the National Bureau of Standards - Annual Report for 1963," miscellaneous publication 255.

NATIONAL BUREAU OF STANDARDS Physical Chemistry Division

John D. McKinley 1/3/64

INTERACTIONS AT GAS-SOLID INTERFACES

This is an experimental program to investigate the various rate processes of importance in chemical interactions at a gas, metal interface. Reactive systems leading to volatile products are studied under conditions of low surface coverage, and particular attention is given to the influence of the crystallographic orientation of the metal surface on the rate processes. Some completed work on energy transfer and kinetics in reactions of halogens with polycrystalline nickel is listed below. This work is being continued on similar systems utilizing ultra high vacuum techniques and large single crystals of nickel with low index planes of known orientation exposed on the surface. Experiments now in progress are an electron microscopic study of the three principal low index planes of known orientation exposed on the surface. Experiments now in progress are an electron microscopic study of the three principal low index planes of nickel at successive stages of reaction with bromine at 700° - 1100°C; a mass spectrometric study of the identity and formation rate of the volatile nickel, chlorine reaction products as a function of the orientation of the reacting surface; a mass spectrometric investigation of the reaction products in the following systems: nickel, fluorine; molybdenum, chlorine; yttrium, chlorine. Planned for the immediate future are further measurements of energy transfer from a hot surface to a cold gas in both reactive and non-reactive systems.

Publications

1. "Translational Energy Accomodation in the Nickel Chlorine Surface Reaction", McKinley, J. Phys. Chem. 66, 554 (1962).

2. "Mass Spectrometric Investigation of the High Temperature Reaction between Nickel and Chlorine", McKinley, J. Chem. Phys. 40, Jan. 1 (1964).

3. "Mass Spectrometric Investigation of the Nickel Bromine Surface Reaction", McKinley, J. Chem. Phys. 40, Jan. 15 (1964).

NATIONAL BUREAU OF STANDARDS Physical Chemistry Division

Pierre Ausloos 1/8/64

RADIOLYSIS OF ORGANIC AND INORGANIC COMPOUNDS

The general objective of this work is to study the fundamental chemistry of radiolytic systems involving hot radical reactions, excited neutral decompositions and particularly ionic processes.

Hot radical studies are now underway on CH_3 species. It is expected that this work will result in publishable results within the next year.

Emphasis is being placed upon ionic reactions. For example, the radiolysis of hydrogen in the presence of a hydrocarbon, RH, is dominated by a very fast proton transfer reaction:

$$H_3^+ + RH \rightarrow RH_2^+ + H_2$$

The relative kinetics of the hydride transfer reaction

$$C_2D_5^+ + HR \rightarrow C_2D_5H + R^+$$

have been measured for about fifteen hydrocarbons and seven other non-hydrocarbon molecules.

An unequivocal demonstration of the production of CH_2 in methane radiolysis with $G \sim 0.35$ at 15 atmospheres has now been obtained.

Research is continuing on solid and liquid phase radiolysis as well as on the effect of applied field on gas phase radiolysis. During the next year, the above research will be continued and the radiolysis of n-pentane and neopentane and the solid and liquid phase radiolysis of propane will be studied.

Publications

1. Lias and Ausloos, "Vapor Phase Radiolysis of Propane-d_8 in the Presence of Other Hydrocarbons", J. Chem. Phys., 37, 877 (1962).

2. Sandoval and Ausloos, "Radiolysis of Propane-d_8 in the Presence of Organic Compounds Other than Hydrocarbons", J. Chem. Phys., 38, 2454 (1963).

NATIONAL BUREAU OF STANDARDS Physical Chemistry Division

Hideo Okabe/James R. McNesby 1/8/64

VACUUM ULTRAVIOLET PHOTOCHEMISTRY

An important class of reactions in radiation chemistry is the production of electronically excited neutral molecules, their modes of decomposition and the subsequent reactions of the fragments so produced. This constitutes the subject matter and the understanding of these processes is the objective. An extension of this research is the study of ionic reactions stimulated by monochromatic photons in the ionizing region.

Chromatically pure light sources have now been achieved for xenon and krypton and H atom resonance lamps and efforts are continuing in the case of the argon resonance lamp. Other significant work in lamp technology is the development of lamps capable of operation up to 400°C with LiF windows.

Photolysis of propylene in the ionizing and non-ionizing region is in progress.

An exchange program has been arranged in which Dr. Okabe, one of the principal investigators, is in Bonn, Germany studying field ion mass spectrometry and Dr. K. H. Welge will spend one year at the National Bureau of Standards establishing a program in vacuum ultraviolet flash photochemistry.

The photochemistry of n-butane has been studied and the details of the photolysis of ethane have been uncovered in an exhaustive experimental study.

Next year's plans include continued efforts to produce an argon resonance lamp and the corresponding study of the photochemistry of propylene in the ionizing and non-ionizing region. The flash photochemical program is expected to give the National Bureau of Standards a capability in the study of excited molecules and radicals produced in vacuum ultraviolet photochemistry. The development of high temperature lamps should enable us to begin a study of the photochemistry of CO_2 or N_2O during the next year.

NATIONAL BUREAU OF STANDARDS Physical Chemistry Division

Vernon H. Dibeler/Robert M. Reese/Henry M. Rosenstock 1/15/64

PHOTOIONIZATION STUDIES

A completely windowless vacuum ultraviolet monochromator combined with a mass spectrometer was recently completed for the study of photoionization processes in low-pressure gaseous systems. The apparatus permits observations in the energy range of ten to twenty electron volts with unequivocal identification of the photoionization products. Preliminary studies have included the determination of the photoionization efficiency curves for acetylene, acetylene-d_2 and benzene and the accurate measurement of their first ionization potentials. Vibrational levels of the ground state ions were also determined. A brief report on the acetylenes has been submitted for publication.

Immediate plans include the determination of ionization efficiency curves for argon and krypton using the high-pressure helium and argon continua as photon sources. Diatomic molecules, H_2, N_2, CO, O_2, and triatomics, particularly those of a related series: CO_2, COS, CS_2, H_2S, H_2O, etc., will be examined in the near future. Particular attention will be paid to molecules for which the calculation of Frank-Condon factors is deemed feasible.

Studies of more complicated series; e.g., methanol and substituted alcohols and thiols, methyl amine and substituted amines, acetylenic and aromatic series are further contemplated. The presence of electronically excited states, auto-ionization and other phenomena are already known to complicate the ionization efficiency curves and the use of homologous series such as above is expected to aid in the identification of these processes.

NATIONAL BUREAU OF STANDARDS Physical Chemistry Division

Louis J. Schoen/D. E. Mann 1/3/64

FLASH SPECTROSCOPY

The objective of the proposed research is the extension of flash photolytic spectroscopy to species isolated in matrices at liquid helium temperatures. Matrix isolation coupled with infrared detection has proved to be an effective and general means for the preservation and study of various radical species whose spectra cannot be obtained in other ways. This applies especially to radicals and molecules which do not have banded or discrete electronic spectra. Flash photolysis, while a powerful means of producing radicals, cannot be successfully applied in cases where the resulting fragments do not have suitable electronic absorption spectra. The aim of the present research is to wed these techniques. The parent substance is deposited along with a large excess of an inert gas such as argon as a thin film on a transparent disk kept near 4^{o}K. The resulting matrix is then subjected to flash photolysis over a period of 10-30 microseconds, with an electronic absorption spectrum being taken within a few microseconds of the peak of the light pulse. If a spectrum is found it will make possible also a study of the deactivation, decay, and diffusion of the fragments in the matrix. Whether or not an electronic spectrum is not found, the matrix will make possible subsequent infrared spectroscopic studies of the fragments to indicate if recombination or reaction has occurred. This approach has the advantage that species, such as high temperature molecules, which cannot be studied by conventional flash photolytic techniques are made accessible to investigation. Preliminary studies have indicated that stray and scattered light will not prove to be a serious problem, and the projected investigation of selected group III, IV, and V halides can be undertaken.

NATIONAL BUREAU OF STANDARDS Heat Division

Joseph Hilsenrath 1/7/64

DATA OF STATE FOR GASEOUS FLUORIDES

The objective of this work is the experimental determination of the pressure-volume-temperature relations in gaseous fluorides and other related halogen compounds. Also, complete tables of real-gas thermodynamic properties from the PVT data and ideal gas thermal functions from spectroscopic and molecular data are being calculated.

Measurements are now underway in a Burnett-type apparatus of the compressibility isotherms for gaseous BF_3. The apparatus is capable of attaining temperatures from 25°C to 200°C and pressures from 5 to 250 atmospheres. Approximately 8 isotherms will be measured during the next six months.

These data will be fitted to a suitable potential function from which will be computed the virial coefficients and their derivatives. The virial coefficients will be used to calculate gas-imperfection corrections to the thermodynamic properties. In the latter part of the year p-v isotherms will be measured on a second apparatus on liquid and gaseous hydrogen fluoride (HF). These data will be combined with similar measurements in the literature and incorporated in a comprehensive correlation of all pertinent available experimental data to determine the degree of association of hydrogen fluoride vapor over a range of temperatures and pressures. Use will be made, in correlating the data, of a new general purpose computing program which permits a deeper diagnosis and analysis than was possible heretofore.

NATIONAL BUREAU OF STANDARDS Heat Division

R. Piccirelli/M. Green/M. Boyd/J. Sengers 1/10/64

MOLECULAR THEORY OF TIME - DEPENDENT PHENOMENA

In the field of statistical mechanics of dense gases, it is proposed to compute the first density coefficient of viscosity and thermal conductivity for some simple molecular models beginning with the hard sphere model. In addition a re-examination of the Chapman-Enskog method as applied to dense gases is being made. It is proposed also to examine the autocorrelation expressions for transport coefficients to see what can be learned from them about very dense gases transport coefficient >300 Amagat.

A priori quantum mechanical calculations of wave functions, energies, and potential curves by means of the linear-combination-of-atomic-orbitals, self-consistent-field method of Roothaan are in progress. These studies are being made on some small unstable molecules, both known and hypothetical (i.e., HO_2, NCl, AlN). Excited states as well as ground states will be studied in an attempt to elucidate the behavior of atoms and small molecular systems in interaction.

Publication

1. Green and Piccirella, "Basis of the Functional Assumption in the Theory of the Boltzmann Equation", Phy. Rev. 132, 1388 (1963).

NATIONAL BUREAU OF STANDARDS Atomic Physics Division

D. R. Lide, Jr./W. J. Lafferty/W. B. Olson 1/7/64

INFRARED SPECTRA AND MOLECULAR CONSTANTS OF DEUTERATED MOLECULES

The purpose of this program is to determine with high accuracy the molecular constants of certain deuterated molecules from measurements of high-resolution infrared absorption spectra. The comparison of constants of deuterated and normal molecules gives considerable information on molecular structure-interatomic distances, angles, vibrational force constants, etc. Furthermore, the results of such measurements are necessary for the calculation of ideal gas thermodynamic properties. The present program is directed particularly toward the investigation of certain light, symmetric molecules, which are not accessible for study by other techniques such as microwave spectroscopy, but which are of great importance.

Work is now in progress on normal and deuterated species of methane, acetylene, allene, and diborane. The many resonances encountered in the higher vibrational levels of these molecules are being analyzed in detail. The objective is to build up as complete information as possible on the pattern of energy levels in these molecules, and then to obtain the most accurate values of the fundamental vibrational and rotational constants.

Publications

1. Olson, Allen, and Plyler, "Analysis of Two Infrared Bands of CH_2D_2", J. Res. Nat'l. Bureau Stds. 67A, 27 (1963).

2. Lafferty and Plyler, "Infrared Spectrum of the $Z_2 + Z_6$ Band of $C^{13}C^{12}H_6$", J. Res. Natl. Bureau Stds. 67A, 225 (1963).

3. Lafferty, Plyler, and Tidwell, "Infrared Specturm of Acetylene-d_1", J. Chem. Phys. 37, 1981 (1962).

4. Lafferty and Plyler, "Molecular Parameters of Ethane", J. Chem. Phys. 37, 2688 (1962).

NATIONAL BUREAU OF STANDARDS Metallurgy Division

Abner Brenner/Sara L. Catey 1/8/64

ELECTROCHEMICAL CALORIMETRY

This program deals broadly with the heat effects attending the passage of the electric current across interfaces involving electrolytes. The first topic studied dealt with the calorimetric measurement of enthalpy changes of electrochemical reactions. The second topic studied dealt with the calorimetric determination of half-cell entropies.

The present activity deals with the measurement of the reversible heat effect attending the passage of an electric current across a liquid junction. The experiments involved the measurement (with minute thermistors) of the temperature change at various distances from the junction of the electrolytes, so as to yield a temperature profile of the effect. The total reversible heat effect has been calculated from the integrated area under the curve of temperature profile (which had been corrected for the Joule heat) and reported as a voltage-equivalent. It has been shown to be independent of the current density or sharpness of the junction and to be related to the Peltier effect and to the diffusion liquid junction potentials.

The following values were obtained for three systems of electrolytes:

0.04 M hydrochloric acid and 0.4 M hydrochloric acid, 30 mv
0.90 M hydrochloric acid and 3.0 M potassium chloride, 80 mv
1.15 M hydrochloric acid and 1.21 M lithium chloride, 80 mv

The future work will deal with (1) determination of voltage-equivalents for a number of systems of electrolytes; (2) measurements of voltage-equivalents for systems of a reversible electrode immersed in an electrolyte; (3) measurement of the temperature coefficients of the EMF of thermocells and of liquid junctions corresponding to the systems involved in items (1) and (2).

Publication

1. Sherfey*, "Calorimetric Determination of Half-Cell Entropy Changes", J. Electrochem. Soc. 110, 213-221 (1963).

*Present address: National Aeronautics Space Administration, Goddard Space Flight Center, Greenbelt, Md.

NATIONAL BUREAU OF STANDARDS Metallurgy Division

Abner Brenner/William H. Metzger, Jr. 1/8/64

CALORIMETRIC DETERMINATION OF THE COMPOSITION AND OF THE EQUILIBRIUM CONSTANT OF COMPLEXES EXISTING IN FUSED SALTS

A calorimeter has been constructed for measuring heats of reaction in fused salt systems at temperatures up to about 850°C. It consists of two individually controlled, concentric heating systems, each provided with a heavy copper or silver cylinder for equalizing the temperature. The temperature of the inner heating system acts as the environment for the calorimeter and is controlled automatically with a precision of about 0.01°C.

The procedure involves the measurement of the heat effect attending the addition of about 1 g of salt, either A or B, to melts composed of various proportions of A and B. The partial molal heat effect is calculated and plotted against the composition of the melt. The heat effect goes through a rapid change in the neighborhood of the stoichiometric composition of the complexes which are formed. The composition of the complex is ascertained from the partial molal heat effects, and the instability constant is calculated from the value of the heat effect and the slope of the curve where it passes through a stoichiometric composition.

This is a general method. To test it, the system cadmium chloride-potassium chloride was investigated because the salts are readily obtained and melt without decomposition. The current experiments are being performed at 800°C, because at this temperature potassium chloride is liquid, and its heat of fusion is, therefore, not involved. The data are not complete but they definitely indicate that two complexes exist in the molten mixture.

Future work will be directed toward completing the work with the system at 800°C and repeating the work at 600°C and perhaps in the presence of an inert fused solvent. The procedure will then be applied to other systems in which there is current interest, for example, titanium halides in fused alkali halide melts or aluminum oxide in cryolite.

NATIONAL BUREAU OF STANDARDS Physical Chemistry Division

D. D. Wagman/V. B. Parker/W. H. Evans/I. Halow 1/10/64

COLLECTION, ANALYSIS, AND COMPILATION OF CHEMICAL THERMODYNAMIC DATA

The preparation of the manuscript for a comprehensive review of data on heats of solution, dilution, and heat capacity for uniunivalent electrolytes in aqueous solution has been completed and is now being readied for publication.

We are continuing to work intensively on the comprehensive review of the chemical thermodynamic literature. This project is reviewing simultaneously all available data on the heats and free energies of formation and heats and entropies of phase change (fusion, vaporization, etc.), and selecting a set of self-consistent "best" values for these quantities. An annual summary of current published literature indexed as to substances and properties measured in the area of chemical thermodynamics is also being prepared as part of the new Bulletin of Thermochemistry and Thermodynamics.

The recalculation to standard units and conditions of all published data on heats of combustion of organic compounds is continuing and will soon be completed. The resulting tables will then be prepared for publication.

SECTION 7

UNIVERSITY OF NOTRE DAME - RADIATION LABORATORY

7-1 The CH_2 and the NH Free Radical

7-2 Vacuum Ultraviolet Photochemistry

7-3 Radiation and Photochemistry of Organometallic Compounds in Benzene

7-4 CO^{60}-Gamma Radiation Induced Cis-Trans Isomerization of Stilbene in Benzene

7-5 Effect of Density in Radiolysis of Ammonia

7-6 Effect of Density on Radiolysis of Ethane

7-7 Radiation and Photochemistry of Group IVB Metal Alkyls in Benzene and Cyclohexane

7-8 Specific Rates of Energy Transfer in Organic Liquid and Rigid Media

7-9 Development of an Accurately Reproducible, Pulsable, UV Source

7-10 Measurement of Luminescence Decay Time After Pulsed UV Excitation

7-11 Luminescence of Pure Hydrocarbons After Gamma-Irradiation at Low Temperature: Spectra of Short-Lived Emission Processes

7-12 Kinetic ESR Studies of Organic Radicals Produced by High-Energy Irradiation

7-13 Luminescence Decay Times

7-14 Application of Laser Techniques in Radiation Chemistry

7-15 Electron Impact Technique for Measuring Ion Excitation and Fragmentation

7-16 Cations, Anions, Radicals and Electrons in γ-Irradiated Organic Glasses at -196°

7-17 Fundamental Nature of Excited Electronic States

7-18 Theoretical Study of Positive and Negative Ions in the Gas Phase

SECTION 7 Continued

7-19 Track Reactions of Radiation Chemistry

7-20 Energy Transfer and Molecular Motions

7-21 Stored Energy and Its Influence on the Catalytic Activity of Platinum

7-22 Effect of Internal Interfaces Upon Formation of Color Centers in Alkali Halides

7-23 Stresses Induced by Oxygen Adsorption on Metallic Oxides

7-24 Formation of Spinels in Metallic Oxides

7-25 Study of Free Radicals

7-26 Liquid Phase Molecular Diffusion Coefficient of Methane in Dilute Solutions

7-27 Free-Radical Aromatic Substitution

7-28 Sterochemistry in Lithium Aluminum Hydride Reduction

7-29 Mossbauer Effect in Sn(II) Complexes

7-30 Determination of Extent of Dissociation in Solution of Complexes of Metal Halides with Aryl Amines

7-31 Infrared Spectra of Complexes of Metal Halides with Ligands Containing the P=S Bond

7-32 Kinetics and Equilibria in Isomerization of α-Branched Trialyklboranes and in Redistribution Reactions Among Unsymmetrical Primary Trialylboranes

7-33 Polarographic and Other Behavior of Simple Ions and Complex Compounds in Dioxane-Water Media

7-34 Relative Lewis Acid and Lewis Base Strengths from PMR Measurements

7-35 Chelates of Polyfunctional Ligands

7-36 Organogermanium Chemistry

7-37 Electrochemical Behavior of Metal Ions in Sulfuric Acid Medium

SECTION 7 Continued

7-38 Development of New Fluorometric Methods for the Determination of Metal Ions

7-39 Infrared Absorption Studies

For further information on completed work, the reader is referred to the open scientific literature.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

Milton Burton/Ko Taki 12/13/63

THE CH_2 AND THE NH FREE RADICAL

There are numerous reports of the role of the free CH_2 radical in electrical discharge in methane*, in photochemistry of diazomethane and of ketene,** in the near uv, and in photochemistry of methane in the far uv and implications of its corresponding significance in radiation chemistry. Similarly, there have been some less extensive studies of NH. Both free radicals can exist in the singlet as well as in the triplet state. Both may participate in hydrogen extraction reactions as well as in insertion reactions; CH_2 has been shown to add an H_2 (or D_2) molecule in a single elementary process. However, some contradictory statements regarding the reactions of these radicals particularly with smaller molecules (e.g. methane) are in the current literature. It is planned to resolve some of the questions thereby created by comparison studies of the reactions of the same free radicals produced from different compounds by different processes. Numerous preliminary experiments with electrical discharge processes have been completed.

* Wiener and Burton, J. Am. Chem. Soc. 75, 5815-23 (1953)

** Chanmugam and Burton, J. Am. Chem. Soc., 78, 509-19 (1956)

Milton Burton/A. D. Kennedy/D. B. Peterson 12/10/63

VACUUM ULTRAVIOLET PHOTOCHEMISTRY

This project is presently in the very early stages of development. Lamps and associated equipment are being constructed which, when complete, will make it possible to investigate photochemical and luminescent systems at wavelengths as short as 1236Å.

It is anticipated that ammonia and cyclohexane will be among the first photochemical systems to be investigated. These two systems are of particular interest because of extensive information available from radiation chemical studies which have been carried out in this and other laboratories. When possible, photochemical results will be compared with those obtained with high-energy radiation.

Also, with this equipment it will be possible to investigate energy transfer processes from higher excited states of molecules such as benzene. Such studies will be a valuable adjunct to the investigations of energy transfer presently being carried out in this laboratory.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

D. B. Peterson/Milton Burton/D. A. G. Walmsley/T. Arakawa 12/16/63

RADIATION AND PHOTOCHEMISTRY OF ORGANOMETALLIC COMPOUNDS IN BENZENE

A detailed study of high-energy (Co^{60}-gamma) and uv-induced decomposition of organometallic compounds of the type $M(C_6H_5)_n$, where M is a Group IVA or Group VA metal in dilute benzene solution is presently nearing completion. Direct photochemical decomposition of these compounds at 2537Å in an inert solvent, (cyclohexane) has also been investigated.

Results obtained are comparable with those obtained for other organometallic compounds used to quench high-energy induced luminescence of organic scintillators in benzene. In luminescent systems the important processes involve energy transfer from solvents to scintillator X (with resultant protection of the solvent) or to quencher D (also with protection of the solvent) and with possible sensitized decomposition. When S is benzene, the excited state responsible for luminescence is $^1B_{2u}$, the first excited singlet, and the quenching processes of interest are those involving that state. Deactivation of excited scintillator by the organometallics has been shown to be unimportant.

In chemical studies, the interaction of the quencher with the system is followed by determination of products of quencher decomposition.

Results obtained thus far indicate that kinetic parameters are the same in luminescence quenching and photosensitized decomposition of the organometallics but different from those obtained in high-energy sensitized decomposition.

Publication

1. Kropp and Burton, "Effect of Added Quenchers in Organic Scintillator Solutions: Organometallics," J.Chem. Phys. 37, 1752 (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

D. B. Peterson/Milton Burton/S. Srivastava 12/10/63

CO^{60}-GAMMA RADIATION INDUCED CIS-TRANS ISOMERIZATION OF STILBENE IN BENZENE

Recently Cundall in England and Kaufman and Hamill in this laboratory have shown that butene-2 undergoes a radiation-sensitized cis-trans isomerization which is most easily interpreted in terms of the following reactions.

$$B \rightsquigarrow B^3$$

$$B^3 + C_4H_8 \rightarrow C_4H_8^* + B$$

$$B^3 \rightarrow B$$

where B^3 is a triplet state of benzene.

From their results they estimate a G of benzene triplets of about 4 or 5. This result is of sufficient importance to warrant further examination. It has been shown that cis-trans isomerization of stilbene can be photosensitized by a number of different donor molecules. This photosensitized isomerization is apparently induced by donor molecules excited to triplet states. Thus, studies of photosensitized and high-energy induced isomerization of stilbene in benzene solution should provide further evidence for the role of triplet states in the radiolysis of benzene.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

D.B. Peterson/P.A. McCusker/Sr. C.M. Wodetzki/M. Nishikawa 12/16/63

EFFECT OF DENSITY IN RADIOLYSIS OF AMMONIA

A number of interesting phenomena are expected to influence the radiolysis of gaseous systems as the density is increased from that characteristic of a gas at one atmosphere to pressures approaching those characteristic of liquids. Among these are collisional stabilization of excited ions and molecules and ion-clustering.

In a previous study in this laboratory, it was shown that $G(H_2)$. and $\underline{G}(N_2)$ from radiolysis of NH_3 undergo marked decreases at pressures well below the critical pressure and approach values characteristic of the liquid phase. These results, which were obtained at a temperature slightly above the critical temperature, are consistent with the formation of clusters of neutral molecules about ions, a phenomenon which has been treated theoretically by Magee and Funabashi of this laboratory. Studies of ammonia at high pressures have been extended to other temperatures and the influence of added scavengers has been examined.

Studies of the effect of density have now been extended to temperatures in the range 100-150°C. Yields of H_2 and N_2 decrease with decreasing temperature but the density at which yields of H_2 and N_2 begin to drop is relatively insensitive to temperature. A temperature effect might have been expected if cluster formation is responsible for the density effect. As part of this investigation some experiments have been carried out to obtain evidence bearing on the details of ammonia radiolysis.

Studies of the effect of added ethylene at various densities have also been made. The latter studies indicate that at all densities at least 85% of the dissociation is to NH_2+H. Analyses of hydrocarbons formed in the presence of ethylene reveal the presence of small but significant yields of propane. It is possible that the propane arises from the reaction of nitrogen atoms with ethylene to give CH_3 which ultimately appears as propane. Studies of very dilute mixture of hydrazine in ammonia are also being carried out in an attempt to elucidate the radiolysis mechanism.

Publication

Toi, Peterson and Burton, "Effect of Density in Radiolysis of Ammonia," Radiation Research, 17, 399 (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

D. B. Peterson/M. Burton/P. A. McCusker/
Sr. C. M. Wodetzki 12/16/63

EFFECT OF DENSITY ON RADIOLYSIS OF ETHANE

Since it had been found in previous work in this laboratory that the product yields on radiolysis of NH_3 were markedly decreased at higher pressures, a study was undertaken to determine whether similar pressure effects occur in other substances.

Ethane, as a typical hydrocarbon, was chosen for this study. Results obtained thus far indicate that $\underline{G}(H_2)$ for pure ethane decreases at high pressures but the effect is less pronounced that in ammonia. The effect of pressure on the yields of hydrocarbon products is also being studied.

To obtain data pertinent to possible mechanisms of the radiolysis, the effect of radical scavengers, such as ethylene and nitric oxide, on the product yields at various pressures is being studied. Mixtures of C_2H_6 and C_2D_6 are being investigated.

Further evidence bearing on the mechanisms is being obtained from studies on the radiolysis of mixtures of C_2H_6 and C_2D_6 at various pressures.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

D. B. Peterson/P. A. McCusker/Sr. P. J. Zeleznik 12/16/63

RADIATION AND PHOTOCHEMISTRY OF GROUP IVB METAL ALKYLS IN BENZENE AND CYCLOHEXANE

The high-energy (Co^{60}-gamma) and uv-induced decomposition of the tetraethyls of Si, Sn, and Pb in benzene and cyclohexane solutions are being studied to correlate decomposition yields with the efficiencies of these metal alkyls as luminescence quenchers. Similar studies are being conducted with the corresponding metal tetraphenyls. $Si(Et)_4$ and $Sn(Et)_4$ have been found to be poor quenchers of luminescence and to undergo very little sensitized decomposition. In this respect $Si(Et)_4$ resembles $Si\Phi_4$. $Sn(Et)_4$, however, differs from Sno_4 in that it is a much poorer quencher and undergoes much less sensitized decomposition. A comparison of $Pb(Et)_4$ with $Pb\Phi_4$ indicates that the $Pb(Et)_4$ is a relatively inefficient quencher of luminescence and also suffers less sensitized decomposition. Comparison of the tetraalkyls among themselves shows that there is a small increase in the extent of sensitized decomposition in going from Si to Sn and a large increase in going from Sn to Pb.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

M. Burton/P.K. Ludwig/C. R. Mullin/M. A. Dillon 12/12/63

SPECIFIC RATES OF ENERGY TRANSFER IN ORGANIC LIQUID AND RIGID MEDIA

Energy (light, x-rays, beta or gamma radiation) which is deposited initially in one component of certain organic solutions shows up partially as luminescent light emitted from another component. The energy transfer can be described as a result of molecular diffusion, energy diffusion or long range interaction between excited and unexcited molecules. It is the object of a variety of studies to obtain information about the specific mechanisms involved in energy transfer processes for a number of systems and eventually to find generally valid underlying relations. Both steady-state and dynamic methods may be employed. In a steady-state method, the affect of scintillator concentration and of quencher concentration on luminescence intensity is used to give a variety of characteristic parameters and ultimately, in conjunction with information from decay time studies, to give certain specific rates for energy transfer and quenching processes. In this work, particularly on solutions containing cyclohexane and benzene as solvent, some relatively high specific rates have been calculated. It is shown that certain high rates, $> 10^{10}\underline{M}^{-1}\text{sec}^{-1}$, are consistent with the best known values of diffusion constants and molecular diameters. Examination of these specific rates in terms of a recently developed theory by Yguerabide, Dillon and Burton, indicate that mechanisms of energy deposition and transfer in cyclohexane and in benzene are radically different.

7-9

UNIVERSITY OF NOTRE DAME Radiation Laboratory

J. T. D'Alessio/P. K. Ludwig/M. Burton 12/12/63

DEVELOPMENT OF AN ACCURATELY REPRODUCIBLE, PULSABLE, UV SOURCE

One of the difficulties in study of excitation transfer processes excited by high-energy radiation resides in recognition of the excited states actually involved. In principle, it should be easy to simplify the problem by exciting specific states with uv-light. The difficulty is that suitable uv lamps for this purpose do not exist. They either have too long a decay time or have non-reproducible decay time characteristics or both. In this laboratory, we have developed a highly reproducible spark-type mercury hydrogen lamp in which the half-width of the light is less than a nanosecond, the decay time is of the order of a half-nanosecond, and the decay curve can be reproduced within a time resolution of less than 0.1 nanoseconds. This lamp and its associated electronic circuit will be described in a forthcoming article.

7-10

UNIVERSITY OF NOTRE DAME Radiation Laboratory

P. K. Ludwig/J. T. D'Alessio/M. Burton/M. A. Dillon 12/13/63

MEASUREMENT OF LUMINESCENCE DECAY TIME AFTER PULSED UV EXCITATION

Uv-excitation of specific excitation levels provides an especially useful tool for examination of the mechanism of excitation transfer in condensed systems. In projected work, it is expected to use the new mercury-hydrogen spark lamp developed by Dr. D'Alessio in the Radiation Laboratory as well as a luminescent source of uv. It has been found by Ludwig and Dillon that 4-bromo-p-terphenyl dissolved in benzene provides a luminescence source of wavelength near 4000Å with a decay time of the order of 0.5 nanoseconds. This source is very reproducible when excited by x-rays and can therefore be used for the purposes of excitation of other systems, e.g., of perylene, dissolved either in liquid solutions or in plastic. These new types of illumination make possible decay time studies which have not hitherto been possible.

7-11

UNIVERSITY OF NOTRE DAME Radiation Laboratory

P. K. Ludwig/M. Burton/M. A. Dillon/M. Kawanishi/R. Rein 12/13/63

LUMINESCENCE OF PURE HYDROCARBONS AFTER GAMMA-IRRADIATION AT LOW TEMPERATURE: SPECTRA OF SHORT-LIVED EMISSION PROCESSES

Theoretical considerations predict a temperature effect on the luminescence properties of condensed systems. Luminescence studies in the low temperature range, were made and background properties of pure aliphatic hydrocarbons after gamma irradiation were examined. It was found that such systems were luminescent and that the only effect of a variety of additives including both scintillator and quencher was to decrease the luminescence intensity. This result was found in the particular case of 3-methylpentane which can be made into a glass near liquid-nitrogen temperature. In a glassy state, light is emitted immediately after gamma irradiation; light emission persists for long periods of time and the rate of light emission can be influenced both by temperature increase and irradiation with suitable wavelengths. Two types of radiation emission have been observed, one with an activation energy near 0.1 ev and the other with an activation energy near 0.25 ev. It is planned to establish the associated spectra and to examine in much greater detail the kinetics of the processes involved.

7-12

UNIVERSITY OF NOTRE DAME Radiation Laboratory

P. K. Ludwig/M. Burton/D. Spence 12/12/63

KINETIC ESR STUDIES OF ORGANIC RADICALS PRODUCED BY HIGH-ENERGY IRRADIATION

Modified ESR (electron spin resonance) equipment is available for use to determine the nature of radical species produced by electron bombardment of organic systems. It will find particular use for radiochemical work such as on the luminescence of Pure Hydrocarbons described above. Modifications of the ESR equipment for use in connection with a Van de Graaff generator involved considerable efforts in the design of suitable waveguides and microwave cavities to meet requirements of high vacuum tightness, high Q-value, temperature control and efficient electron beam penetration. To extend its use to kinetic studies the electronic sampling technique developed by Dreeskamp and Burton is being adapted to follow the decay of radicals with lifetime down to the order of microseconds. Future application of the ESR equipment includes the study of excited states, a potentially powerful tool when used in connection with a laser providing an extremely high density of radiation.

LUMINESCENCE DECAY TIMES

1. FLUORESCENT DECAY TIME MEASUREMENTS AFTER PULSE EXCITATION

M. Burton/P. K. Ludwig/R. Povinelli/Sr. S. Kennard 12/12/63

The dynamic method of approach to the problem of energy transfer in organic liquid and rigid media involves a determination of rise and decay characteristics of the luminescence of a system after extremely short excitations. The method employed in such work was developed in this laboratory and is described in previous publications. There have been recent improvements which enable sharp demarcation between different mechanisms of light emission. At present, characteristic decay times (there are usually two of them) have been established for scintillator solutions containing six different scintillators in three different liquid solvents and in polystyrene. A comprehensive table of results will be published shortly. This work is an extension and improvement on results previously reported.

Publication

1. Yguerabide and M. Burton, "Luminescence Decay Times: Concentration Effects", J. Chem. Phys. 37, 1757-1774 (1962).

2. TRANSFER PROCESSES IN RIGID MEDIA: TREATMENT OF ENERGY

P. K. Ludwig/M. Burton/M. A. Dillon 12/13/63

Examination of the theory of excitation transfer and quenching in luminescence systems indicates that it is diffusion-controlled. However, the rules of diffusion-control should be different for photochemical excitation and for high-energy excitation and should also be affected by the nature of the diffusion-controlled process -- whether it involves actual molecular diffusion or diffusion of excitation (cf. J. Yguerabide, M. Dillon and M. Burton, paper submitted for publication). The Dreeskamp-Burton method of decay-time studies (Dreeskamp, Ghosh and Burton, Rev. Sci. Instr. 32, 304-307 (1961)) as improved by P. K. Ludwig, makes possible the very accurate observation of decay curves. At present a systematic study is being made of a variety of scintillators dissolved in plastic media. Certain rather curious results indicate that the behavior of rigid systems is not readily predictable from studies of liquid phases.

3. EFFECT OF TEMPERATURE ON LUMINESCENCE DECAY TIMES

P. K. Ludwig/M. Burton/E. Gruenhut 12/13/63

It is known from theoretical considerations that the excitation transfer mechanisms in organic liquid and rigid media should be affected by temperature. However, little attention has been paid to this subject because of the difficulty of measuring decay times themselves. Development of satisfactory techniques of decay time measurements, described above, encourages the expectation that it is now time to measure temperature effects. Suitably modified decay-time equipment is now in the process of construction and will be used for study of the effect of temperature on decay times.

4. EFFECT OF PHYSICAL STRAIN ON LUMINESCENT DECAY TIMES

P. K. Ludwig/M. Burton 12/13/63

If the structure of the medium plays a significant role in the establishment of excitation transfer mechanisms in rigid media particularly, stresses brought to bear upon the system should change the strucutre and thus affect the significant specific rates. The Dreeskamp-Burton technique, as modified by Dr. Peter Ludwig and others in this Laboratory, is being subjected to further modification which will permit the application of physical stresses to the scintillating medium. It is expected that this work will take a long time but it seems to be both desirable and necessary.

5. EFFECT OF VISCOSITY AND SOLVENT ON LUMINESCENCE DECAY TIMES AND LIGHT YIELDS IN LIQUID ORGANIC SYSTEMS

P. K. Ludwig/M. Burton/R. Povinelli 12/13/63

The elaborate theory of quenching and excitation transfer processes has developed by Yguerabide, Dillon and Burton (paper submitted for publication) suggests that viscosity should have a significant effect on fluorescent decay times and light yields. The modified Dreeskamp-Burton method of decay time measurement is being used to study the effect of viscosity in a variety of scintillating systems and also the possible effect of nature of the exciting radiation.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

Peter K. Ludwig/Milton Burton 12/12/63

APPLICATION OF LASER TECHNIQUES IN RADIATION CHEMISTRY

The application of lasers to sources of coherent and extremely intense light in the work of this laboratory may open a vast area of research. The mechanisms of excitation of various organic systems under the light conditions of a laser are not well understood. Studies of this kind may well contribute to a better understanding of the basic processes of light absorption. Further work will therefore be particularly directed towards the application of lasers as light sources. It is too early to predict the nature of the results which may be obtained but it is an important objective of the proposed work to obtain fairly uniformly distributed excited solute molecules in reasonably high concentration in a large volume of solvent. A technique of this nature will assist both radiation chemical and photochemical studies. It is premature to discuss some attendant theoretical objectives.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

W. H. Hamill/W. P. Hauser/S. Tsuda/G. F. Hennion, Jr. 12/11/63

ELECTRON IMPACT TECHNIQUE FOR MEASURING ION EXCITATION AND FRAGMENTATION

Several laboratories have reported finding structure in ionization efficiency (IE) curves by the retarding potential difference method (RPD) which correlates with observed spectroscopic molecular ion and fragment ion states. Other IE curve structure corresponds to ion-pair formation. Substantially all of this work concerns atoms and diatomic molecules.

Work in progress in the Radiation Laboratory at Notre Dame discloses more structure for simple ions (e.g., O_2^+, CH_4^+) than others have hitherto reported. For $C_2H_4^+$ from C_2H_4, C_2H_6, C_3H_8, C_4H_{10} there is always the same structure. Similarly for CH_3^+ from CH_4, CH_3Cl etc., for $C_2H_5^+$ from C_2H_6, C_2H_5Cl etc. etc. The cross-section for $RH \rightarrow R^+ + H^-$ approximates that for $RH \rightarrow R^+ + H$, not previously reported, and greatly exceeds that for $RX \rightarrow R^+ + X^-$ (X = halogen). When R_e^+ (excited) forms, all $R_e^+X^-$ and R_e^+X pairs are detected.

Most unexpectedly, the IE curve for RX^+ always shows structure at the onset for R^+X^-. Presumably $RX + e \rightarrow RX^* + e$; $RX^* \rightarrow RX^+ + e$ and also $RX^* \rightarrow R^+X^-$. Present theory does not explain this.

This line of investigation is continuing. It will include re-examination of all thermochemistry by electron impact.

Publications

1. Van Dusen, Jr. and Hamill, "Ionix and Free Radical Processes in the Radiolysis and Sensitized Photolysis of Benzene Solutions," J. Am. Chem. Soc. 84, 3648 (1962).

2. Nash and Hamill, "The Effect of Hydrogen Iodide on the Radiolysis of Cyclohexane-d_{12}," J. Phys. Chem., 66, 1097 (1962).

3. Theard and Hamill, "The Energy Dependence of Cross Sections of Some Ion-Molecule Reactions," J. Am. Chem. Soc., 84, 1134 (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

W. H. Hamill/M. Kondo/J. B. Gallivan/D. Skelly 12/11/63

CATIONS, ANIONS, RADICALS AND ELECTRONS IN γ-IRRADIATED ORGANIC GLASSES AT -196°

An original technique for examining by spectrophotometry the major transient intermediates from many γ-irradiated organic glassy systems has been developed at Notre Dame. Behavior of cations and anions produced by γ-irradiation was established by comparison with chemically prepared authentic ions (e.g., $C_{10}H_8^-$ and $NH_2C_6H_4N(CH_3)_2^+$).

Dissociative electron attachment, solvent-solute positive charge exchange, proton transfer and photodetachment of electrons have been observed and are under continued study. The measurement of electron affinity from a photodetachment spectrum in nonpolar medium is being examined. The chemical effects of ion recombination are being examined by observing reactants, as cyclo-$C_6H_{10}^+$ + e^- (trapped), then photodetaching the electron and observing product $C_6H_8 + H_2$. Only H_2 is not measurable in the glass at -196°. G(e^- -delta) will be measured as $(C_6H_5)_2^+$ at very small solute concentrations. Luminescence spectra and intensities from ion recombination by photodetachment of trapped electrons at various frequencies are being measured. With solutes, the known solute phosphorescent spectrum is emitted. Effects of second solutes (e.g., electron attachment, proton abstraction) will be studied by this very sensitive method.

Publications

1. Guarino, Ronayne and Hamill, "Solute Competition for Thermal Electrons in Gamma-Irradiated Organic Glasses at -196°", Radiation Research, 17, 379 (1962).

2. Ronayne, Guarino and Hamill, "Electron Attachment and Solvation in Gamma Irradiated Organic Glasses", J. Am. Chem. Soc., 84, 4230 (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

John L. Magee/J. D. Mitchell 12/11/63

FUNDAMENTAL NATURE OF EXCITED ELECTRONIC STATES

The initial absorption of energy from high-energy particles in matter is in the form of electronic excitation. The theoretical group has been interested in the description of electronic states of irradiated matter from the time of the initial energy deposition through its various transformations and migrations. A problem of particular interest is the behavior of low-energy excited states which can be treated as separated electron-positron pairs of charged particles. We hope that this study will help us understand the size and form of tracks (spurs for low-LET radiation). We have found the study of one-dimensional models useful and we expect to be able to generalize results to real materials of interest, such as liquids and glasses. A report on this work should be available within six months.

Publication

Chen and Magee, "Excitation of Molecular Vibration by Slow Electron Impact," J. Chem. Phys., 36, 1407-1411 (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

J. L. Magee/Fueki/A. Mozumder/Mo. F. M. Schmitt 12/11/63

THEORETICAL STUDY OF POSITIVE AND NEGATIVE IONS IN THE GAS PHASE

The structure of both positive and negative ions is of obvious interest in radiation chemistry. They are also of interest in connection with current work in mass spectrometry being conducted in the Radiation Laboratory.

The complete spectrum of the excited state of the lower hydrocarbon molecules (to $C_{10}H^{+}_{2n+2}$) is being studied by a semi-empirical method developed by Dr. Fueki. A computer program for obtaining these energies has been developed and debugged. Within the next six months a report on this work will be available.

The structure of negative ions has been of interest to the theoretical group for some time. We are interested in negative ions formed by attachment of an additional electron to neutral molecules with the binding due to secondary (i.e., dipolar and polarizability) interaction, and also excited states arising from two-electron excitations. Computer programs are being developed for both of these types of ions and results should be obtained within the next year.

We hope to extend this work to the reactions of ions.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

John L. Magee/Kenji Fueki 12/11/63

TRACK REACTIONS OF RADIATION CHEMISTRY

The reactions of long-lived intermediates such as radicals and ions in particle tracks is a problem of continuing interest in the theoretical group. A rather extensive study of track reactions involving the numerical solution of ten coupled inhomogenous partial differential equation was completed and presented at the Notre Dame Discussion of the Faraday Society in September 1963. This work led to a considerable increase in our knowledge of the structure of tracks and brought up questions regarding mechanisms of reaction (such as negative ions with neutral molecules) and questions regarding the mathematics of the set of equations.

At present we are developing programs to study specific effects of the overlapping of tracks and to determine the transient chemical behavior of complex systems such as are obtained by irradiation of gases. We hope that significant progress can be made in this work early in 1964.

Publication

S. G. ElKomoss and Magee, "Parent Ion Recapture in Gases," J. Chem. Phys., 36, 256-262 (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

John L. Magee/Koichi Funabashi 12/11/63

ENERGY TRANSFER AND MOLECULAR MOTIONS

The purpose of this study is to understand the effects of intermolecular electronic interaction on molecular motions, in particular, dissociation processes and, at the same time, to investigate the mechanisms for energy localization. The system under consideration is a linear chain of identical diatomic molecules. The total time-dependent wave function, written as a linear combination of suitable product-form wave functions of time, can be followed by calculating the expectation values for each internuclear separation from the total wave function. The probability and the location of dissociation depend upon the ratio of the interaction energy to the spread of energy in the Franck-Condon region.

It is planned to extend the study to a more general case of mixed systems where impurity effects compete with the effects due to molecular motions in energy trapping. Also, it is hoped to study the effects of multiple exciton bands.

A paper discussing some aspects of this work has been submitted for publication in "Actions Chimiques et Biologiques des Radiations" edited by Professor M. Haissinsky.

Publication

1. Lorquet, ElKomoss and Magee, "Energy Transfer Phenomena and Dissociation Processes in Electronically Excited Molecules," J. Chem. Phys. 37, 1991-2000 (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

J. T. Banchero/J. A. Herbst 12/11/63

STORED ENERGY AND ITS INFLUENCE ON THE CATALYTIC ACTIVITY OF PLATINUM

In Metals, stored energy is usually associated with lattice defects which may be produced, although to different degrees, through cold working, irradiation, quenching, electrodeposition, etc. The classification and behavior of lattice defects, principally through measurements of changes in density, extra-resistivity, hardness, thermoelectric force and the rate of release of stored (strained) energy, has been the subject of considerable research in the past decade. However, the role these lattice defects play in the catalytic activity of a metal has not yet been established conclusively. The purpose of the present study is to establish the nature of the active sites in catalytic platinum; specifically the connection, if any, between these hypothetical sites and point defects (i.e., vacancies) and/or dislocations of pure platinum metal at its surface. Investigations have been made to determine the influence of cold work on the catalytic activity of platinum metal, its activity being probed through the batch wise decomposition of hydrogen peroxide. Reaction rates as a function of the amount of cold work, temperature and hydrogen peroxide concentration were determined via measurement of the rate of oxygen evolution. The influence of neutron and gamma-ray irradiation on the catalytic activity of platinum metal is currently under study.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

G. C. Kuczynski/Charles Gibbon 12/11/63

EFFECT OF INTERNAL INTERFACES UPON FORMATION OF COLOR CENTERS IN ALKALI HALIDES

This is the first part of a study of the mechanism of diffusion of point imperfections in ionic crystals. This part deals with the investigation of the mechanism of formation of color centers such as F, M, N, R and V near the grain boundaries of pure polycrystalline alkali halides samples in presence and absence of ionizing radiation.

It has been found (as reported in previous publications) that the presence of grain boundaries and of radiation capable of ionizing the F centers greatly accelerates diffusion of defects. There is reason to believe that the chemical reactions in the grain boundaries at elevated temperatures, produce a great number of halogen vacancies and some acceptors in the crystal layer adjacent to the grain boundary.

Studies are conducted on bi-crystals as well as polycrystalline samples prepared from fine powder of very pure KCl, pressed and sintered in vacuum. The absorption spectra obtained from these samples yield information about kind and quantity of centers produced during these operations. From the measured bleaching rates information about diffusion of F centers and mutual interaction of color centers will be obtained. In addition, in some of these samples the F centers will be produced by additive coloration and/or irradiation with a Cobalt-60 source. The bleaching of these centers will also be studied.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

G. C. Kuczynski/Norris Hooten 12/11/63

STRESSES INDUCED BY OXYGEN ADSORPTION ON METALLIC OXIDES

The objective of this research is to explore the space-charge layer near the surface of the oxides. Preliminary experiments have indicated that the adsorption of oxygen on the surface of thin plates ($<100\mu$) of MgO crystals produces small changes in the crystal dimensions. This is probably traceable to ionization of the defects near the crystal surface by transfer of their electrons to the adsorbed atoms. (The sizes of ionized and neutral defects are not the same.) Measurements of the strains produced during adsorption and of the optical absorption are expected to yield some information about the number and quality of these imperfections. The whole problem has obvious relation to catalysis.

The dimensional changes at present are measured by electrical strain gages. However, this method is not altogether satisfactory, as the cement used to affix the gage to the surface of the crystal seems to undergo some changes in vacuum. Therefore, in the future, a system will be employed in which a thin crystal plate, rigidly held at one end and with one side covered with a thin layer of gold, will be made a part of a condenser whose capacity will change with the plate deformation.

The point imperfections will be introduced either by heat treatment (deviation from stoichiometry) and/or by irradiation with a Cobalt-60 source.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

G. C. Kuczynski/D. A. Venkatu 12/11/63

FORMATION OF SPINELS IN METALLIC OXIDES

This is the third part of a project dealing with the general problem of diffusion in ionic crystals. Here, the objective is to investigate the diffusive phenomena occurring during the formation of ferrites. Ferrites are usually produced by sintering. The experimental technique used is to measure the size changes of ferrites during sintering and to carry out a detailed microscopic study of the growth of spinel crystal between a sphere and a plate of two different oxides. At present the systems Fe_2O_3-NiO, Fe_2O_3-MgO and MgO-NiO are under investigation. It has been found that the process of sintering is controlled chiefly by interdiffusion; the process may be modified greatly by the stresses set up during the growth of the spinel phase.

During the next year, several other systems, such as Fe_2O_3-ZnO and Cr_2O_3-ZnO, will be studied and efforts will be made to establish a generalized theory of this phenomenon.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

Francis Owen Rice 12/11/63

STUDY OF FREE RADICALS

This project may be divided into two parts, the first of which includes a study of free radicals produced at temperatures in the neighborhood of 2°K. This temperature was selected because it may be of significance as being the temperature of interstellar space. The comprehensive study of free radicals made at the Bureau of Standards some years ago was done mostly at temperatures of 4°K and higher. At these temperatures migration effects are far from negligible so that only very small concentrations of free radicals could be obtained for study.

At temperatures below 2°K, radicals would have to be formed in the matrix from molecules by photochemical decomposition or by radiative decomposition. The radicals produced as well as their life times and reactions would be studied by ESR.

The second line of work would be the study of free radical reactions in which the free radicals are produced by photochemical decomposition by light in the region 1000-2000Å. It seems rather certain that in this region divalent radicals are produced. There are three simple divalent radicals, CH_2, NH, and O. Their reactions with molecules seem to be quite different from those of univalent radicals and depends on the number of electron pairs in the reacting molecule.

A primary study will be made of absorption spectra in this region. It is hoped to find suitable molecules (CO is one) that have banded absorption and therefore permit decomposition or excitation of each species by varying the wavelength of the light.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

James P. Kohn/John Hu

12/11/63

LIQUID PHASE MOLECULAR DIFFUSION COEFFICIENT OF METHANE IN DILUTE SOLUTIONS

The primary objective of the work is the perfection of experimental techniques to measure the diffusion coefficient (in nonpolar systems) as a function of temperature with high accuracy. The molecular diffusion coefficient is calculated from data on total rate of absorption in a liquid phase. The binary systems, methane-n-hexane and methane-3 methyl-pentane have been studied and work is proceeding on methane-n-octane.

The effect of pressure on the diffusion coefficient is studied employing a single phase technique and vessels capable of pressures up to 7000 atm. The system methane-n-hexane has been studied up to 5000 atm.

It is anticipated that the work will lead to a better understanding of molecular diffusion in the liquid state, particularly the role of pressure, temperature and solvent molecular size on the molecular diffusion coefficient.

Publication

1. Shim and Kohn, "Multiphase and Volumetric Equilibria of Methane-n-hexane Binary System at Temperatures between -110° and 150°C," J. Chem. and Eng. Data, I, 3-8 (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

E. L. Eliel/J. Saha 12/11/63

FREE-RADICAL AROMATIC SUBSTITUTION

A reinvestigation was made of the apparent isotope effect in the arylation of benzene-$\underline{d}_1$ with phenylazotriphenylmethanes, $ArN{=}NCPh_3$ and it was confirmed that the isotope effect was unity within limits of experimental error. The isotope effect in the arylation of benzene-d_1 with various diazonium hydroxides was also unity. The tentative conclusion that dihydrobiaryl intermediates are absent in these reactions because of the operation of a cage effect became untenable in the light of reports in the literature that arylclohexadienyl radicals can, in fact, be isolated. The previously studied reaction of nitrosoacetanilides with benzene-$\underline{d}_1$ to give biaryls was therefore also reinvestigated and it was found that here, as well, iodobenzene is obtained in the presence of iodine in low concentration. This makes the operation of a cage effect very unlikely; however, no alternative mechanism is apparent at the present time.

The invariance of the isomer ratio in the phenylation of substituted benzenes (C_6H_5X), in the presence and absence of oxygen has been reinvestigated. To obtain further information, chlorobenzene-$\underline{o}$-d_1 and -$\underline{p}$-d_1 have been arylated; although an isotope effect is found in the arylation of the ortho-deuterium compound (ca. 2.3), the isomer ratio is the same as in undeuterated chlorobenzene. These surprising results are now being evaluated.

Publication

1. Eliel, Eberhardt, Simamura and Meyerson, "Mechanisms of Free-Radical Aromatic Substitution," Tetrahedron Letters, 749, (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

E. L. Eliel/B. Thill/S. Schroeter 12/11/63

STEREOCHEMISTRY IN LITHIUM ALUMINUM HYDRIDE REDUCTION

The stereochemistry of reduction of 3-phenyl-2-butanone and 1,2-diphenyl-1-propanone with lithium aluminum hydride and various mixed hydrides has been investigated. The results may be interpreted in terms of "steric approach control", i.e., the more hindered the reagent, the less it attacks from the more hindered side as defined in the model of this reduction proposed by Cram. The results suggest that Cram's model comes close to representing the actual transition state in the reaction and that Cram's rule is not just an empirical rule but actually rests on a mechanistic foundation.

Experiments are presently underway to study the stereochemistry of reduction of oximes. Preliminary results indicate that oximes are less subject to "product development control" than are the corresponding ketones in reduction with lithium aluminum hydride.

Publication

1. Eliel, Pilato and Badding, "Reductions with Metal Hydrides. XIII Hydrogenolysis of Hemithioacetals and Hemithioketals with Lithium Aluminum Hydride-Aluminum Chloride," J. Am. Chem. Soc., 84, 2377 (1962).

Columba Curran/Walton Welna 12/12/63

MÖSSBAUER EFFECT IN Sn(II) COMPLEXES

The Sn^{119} nucleus has characteristics favorable for Mössbauer studies; the nuclear resonance absorption of a number of Sn(IV) compounds has been studied in other laboratories. Sn(II) complexes are of particular interest in that the tin atom has an unshared pair of valence electrons with appreciable s character. These have a relatively large effect (compared to p and d electrons) on the ground and excited nuclear energy levels. It is to be expected that the interaction of these electrons with the nucleus will vary appreciably with the nature of the groups attached to the tin atom, resulting in a wide spectrum of chemical shifts. Mössbauer studies should be very informative regarding the electron withdrawing and electron releasing properties of the attached ligands.

Very few Sn(II) complexes are reported in the literature. We have prepared a few of these and it is planned to synthesize many more. Types of complexes to be studied include those of tin halides with halide ions and with neutral mono-and bidentate ligands, and those of Sn^{++} with bidentate anions, for example: bis(8-quinolinato)tin (II). We will assemble an instrument for Mössbauer studies during the coming year.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

Columba Curran/Scaria M. Chackalackal 12/12/63

DETERMINATION OF EXTENT OF DISSOCIATION IN SOLUTION OF COMPLEXES OF METAL HALIDES WITH ARYL AMINES

Very few studies have been made of the dissociation of metal complexes in organic solvents. We have previously studied the solid state displacement of aryl amines from their complexes with metal halides by such donor molecules as hexamethylene-tetramine and thiourea. At present the dissociation of these aryl amine complexes is being studied in a variety of organic solvents by infrared absorption (chiefly) and nuclear magnetic resonance measurements.

The NMR (Nuclear Magnetic Resonance) spectra of the coordinated amines have sharp N-H peaks compared to those of the free amines. The chemical shift of the N-H peak appears to be proportional to the extent of dissociation of the complex. Present studies are being carried out in acrylonitrile solutions; they are limited by the low solubility of many complexes.

Infrared studies concentrated in the 3-micron region are being carried out on the absorptions associated with the N-H stretching vibrations of the free and coordinated amines. The amines studied include aniline, p-toluidine, p-anisidine and p-chloroaniline; the metal halides include the chlorides, bromides and iodides of zinc, cadmium, cobalt (II), copper (II), and manganese (II). Dissociation increases with increasing electron withdrawing property of the para substituent, and from chloride to bromide to iodide. It is planned to determine dissociation constants for these complexes at various temperatures. A correlation of the NMR and infrared studies will be made.

Publication

Bro. Curran, "Infrared Spectra of Complexes of Metal Halides with Amines Containing the N-Methyl group," to be published in "Proceedings of International Symposium on Molecular Structure and Spectroscopy" Tokyo, Japan, September, 1962.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

Bro. Columba Curran/Jose Philip 12/12/63

INFRARED SPECTRA OF COMPLEXES OF METAL HALIDES WITH LIGANDS CONTAINING THE P=S BOND

A number of complexes of metal halides with ligands containing the P=O bond have been prepared previously; the electric dipole moments of some and infrared spectra of all of these complexes have been obtained. For comparison, a number of ligands containing the P=S bond have been synthesized: tributylphosphine sulfide, tripiperidinophosphine sulfide and tripyrrolidinophosphine sulfide. Infrared spectra have been obtained and the P=S stretching vibration frequency characterized. It is planned to determine the dipole moments of these compounds to compare the polarities of the P=O and P=S bonds. To date we have been able to isolate pure complexes of only the last two compounds. From solution, complexes with only $CdBr_2$, CdI_2, $ZnBr_2$ and ZnI_2 have been obtained only by solid state reactions. The frequency of the P=S stretching vibration, in the range 590-680 $cm.^{-1}$, is decreased on complex formation. The shift is about 30 $cm.^{-1}$ for tripiperidinophosphine sulfide complexes. Work is continuing in an effort to prepare complexes with other metal halides and with the other ligands that have been prepared.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

P. A. McCusker/Sr. Grace Francis Rossi/Francis X. Mueller 12/11/63

KINETICS AND EQUILIBRIA IN ISOMERIZATION OF α-BRANCHED TRIALKYLBORANES AND IN REDISTRIBUTION REACTIONS AMONG UNSYMMETRICAL PRIMARY TRIALYLBORANES

The work on isomerization kinetics has been carried out for the isomerization of t-butyldiisobutylborane to triisobutylborane and for the stepwise isomerization of triisopropylborane and tri-sec-butylborane through the intermediate unsymmetrical compounds to tri-n-propylborane and tri-n-butylborane. From rate data at several temperatures, energies and entropies of activation have been obtained. These data suggest the conclusion that the mechanism of isomerization probably involves the formation of R_2BH-olefin as the rate-determining step but that the olefin is separated in the case of t-butyldiisobutylborane and remains complexed in the case of the secondary trialkylboranes.

Redistribution of primary alkyl groups in the following type of reaction $R_3B + R'_3B \rightarrow R_2BR' + R'_2BR$ has been shown to be negligible at room temperature but to be quite rapid at 90°C. Preliminary data indicate that a statistical distribution of alkyl groups occurs. The kinetics of the redistribution reaction will be studied to obtain information bearing on the mechanism of the reaction.

Publication

1. McCusker, Pennartz and Pilger, "Organoboron Compounds. XIV. Rapid Alkoxy Exchange between Dialkylalkoxyboranes and Alkyldialkoxyboranes," J. Am. Chem. Soc., 84, 4362 (1962).

UNIVERSITY OF NOTRE DAME Radiation Laboratory

Bro. Columba Curran/Rev. Joseph L. Walter/
Sr. M. Rosalie Urzendowski

12/16/63

POLAROGRAPHIC AND OTHER BEHAVIOR OF SIMPLE IONS AND COMPLEX COMPOUNDS IN DIOXANE-WATER MEDIA

The polarographic study in dioxane-water media was undertaken to note the effects of adding increasing amounts of dioxane upon the limiting current, half-wave potential, diffusion current constant, viscosity, density, etc. of cadmium ion in such supporting electrolytes as 0.1 $\underline{N}$ KNO_3, 0.1 $\underline{N}$ KCl and in 0.1 $\underline{N}$ $NaClO_4$. Experimental data on half-wave potentials and diffusion current constants of Cu(II), Ni(II), Co(II), Zn(II), and Cd(II) in various supporting electrolytes were also determined. The formation constants of several alkylhydroxy substituted pyridines with Cu(II) and Cd(II) were determined polarographically. The acid dissociation constants and chelate stabilities of alkyl-amino, alkylhydroxy and alkyl-carboxy-pyridyl type ligands with simple metal ions were obtained by the potentiometric method. The heat contents of some of these complexes were determined by a direct calorimetric method. From the polarographic and potentiometric results, plus the calorimetric data, thermodynamic values will be calculated.

UNIVERSITY OF NOTRE DAME Radiation Laboratory

P. A. McCusker/J. F. Deters 12/11/63

RELATIVE LEWIS ACID AND LEWIS BASE STRENGTHS FROM PMR MEASUREMENTS

This work involves a survey of the effects of Lewis acid - Lewis base interactions on the chemical shifts of alpha protons in either the base or the acid or both by PMR (Proton Magnetic Resonance) techniques. Results to date have indicated the possibility of developing a quantitative Lewis acid scale based on the change in chemical shift of ether hydrogens in going from the pure ether to the ether-Lewis acid complex. The ratio of changes in chemical shifts of some of the following Lewis acids have been found to be the same for at least two different ethers. The relative Lewis acidities so far measured, based on BF_3, as a standard, are as follows: $Bu_2BCl = 0.74$; $BF_3 = 1.00$; $BuBCl_2 = 1.27$; $AlCl_3 = 1.33$; $BCl_3 = 1.64$. Extensions to a large variety of other Lewis acids is planned.

From selected Lewis acids containing suitable alpha protons it is hoped that a similar Lewis base scale may be developed.

Exchange equilibria data have been obtained for reactions of the following type. $R_2O.\ BF_3 + R'_2O \rightleftharpoons R'_2O.BF_3 + R_2O$. For a number of pairs of ethers the equilibrium constants have been obtained at several temperatures and ΔH^o and ΔS^o values have been calculated.

It is planned to extend these studies to a wide variety of ethers and other Lewis bases.

7-35

UNIVERSITY OF NOTRE DAME Radiation Laboratory

R. S. Bottei/Fr. T. Fangman/W. Joern/D. Quane
R. Schneggenburger 12/11/63

CHELATES OF POLYFUNCTIONAL LIGANDS

Chelates of di-, tri-, and tetra-valent metal ions with the polyfunctional ligands, naphthazarin, β-hydronaphthazarin, β-hydronaphthazarin disulfonate, 2, 5-dihydroxy-1, 4-benzoquinone, dicupferron, and some dicarboxylic acids, are being studied by a variety of methods which include: elmental analysis, visible and infrared spectrophotometry, polarography, and thermogravimetry. Studies on the chelates are directed toward determination of the effect of structural changes in the ligands on composition, reactivity and stability and also the effect of the various metal ions on the thermal stabilities of the chelates should polymers be formed. Some of the work has already been reported.*

Future plans include continuation extension of the work to include other molecules structurally related to those already studied. These may include: 1, 4, 5, 8-tetrahydronaphthalene, naphthadiquinone, dinaphthazarin, di-β-hydronaphthazarin, α- and β-hydrojuglone, purpurin, and reduced purpurin. The photochemistry and radiation chemistry of complexes will eventually be studied.

*"A Spectrophotometric Study of the Thorium- -Hydronaphthazarin Disulfonate System," J. Inorg. Nucl. Chem. 21, 265 (1961).

7-36

UNIVERSITY OF NOTRE DAME Radiation Laboratory

R. S. Bottei/Mr. L. Kuzma 12/11/63

ORGANOGERMANIUM CHEMISTRY

Recently, after a very thorough review of the literature, work was begun on the preparation and disproportionation of organogermanium alkoxides of the type $(RO)_nGe(OR')_{4-n}$. Various combinations of R and R' and their disproportionation at different temperatures will be studied. Some of the techniques to be used will include infrared spectrophotometry, nuclear magnetic resonance spectroscopy, and vapor phase chromatography.

Publication

1. Quane and Bottei, "Organogermanium Chemistry", Chem. Rev., 63, 403-442, (1963).

7-37

UNIVERSITY OF NOTRE DAME Radiation Laboratory

R. S. Bottei/Sr. M. Lawreace Antoun 12/10/63

ELECTROCHEMICAL BEHAVIOR OF METAL IONS IN SULFURIC ACID MEDIUM

Electrochemical studies have been concerned with polarographic behavior of certain metal ions in sulfuric acid of varying concentration (0.1 M to 18 M) and the coulometric generation of Cr^{++} in sulfuric acid medium. As yet the coulometric generation of Cr^{++} has not been attempted, but the polarographic work (which was necessary before attempting the coulometric work) has given some rather unusual results; the half-wave potential shifted as H_2SO_4 concentration was changed and, for a given concentration of acid, the diffusion current increased with time and finally reached a limiting value. More intensive studies are now under way to try to explain the observed behavior.

7-38

UNIVERSITY OF NOTRE DAME Radiation Laboratory

R. S. Bottei/Bro. I. Ambrose Trusk/Mrs. A. D'Alessio 12/11/63

DEVELOPMENT OF NEW FLUOROMETRIC METHODS FOR THE DETERMINATION OF METAL IONS

In the fluorometric studies, a new method has been developed for the determination of tungsten and has been successfully applied to certain non-ferrous alloys. The application of the method to iron alloys requires certain preliminary separations which are now being studied. A new method for the determination of thorium in acid solution has also been developed and its application to a wide variety of substances is under investigation. Future work will concern the development of procedures for elements such as titanium and niobium which have not as yet been determined fluorometrically.

Publication

1. Anal. Chem., "Fluorometric Determination of W with Flavanol," 35, 1910, (1963).

INFRARED ABSORPTION STUDIES

1. COMPLEXES OF TRANSITIONAL METAL IONS WITH GLYCINE, DL-ALPHA-ALANINE, ALPHA-AMINO-ISOBUTYRIC ACID AND DL-ISOVALINE

Bro. Columba Curran/Rev. Joseph L. Walter/J. A. Durkin 12/16/63

The infrared spectra of cis-and trans-isomers of platinum(II), palladium(II), and copper(II) glycine chelates and the trans-complex of nickel(II) have been investigated from 670 to 270 cm^{-1}. Assignments for the observed metal-nitrogen stretching frequencies have been made using an approximate normal coordinate analysis. Approximate metal-nitrogen bands stretching force constants were calculated for the trans-compounds and found to vary in the order Pt(II) > Pd(II) > Cu(II) > Ni(II), thus demonstrating a corresponding order for the relative strengths of the metal-nitrogen interaction. A paper entitled "Infrared Absorption Spectra of Metal-Amino Acid Complexes. II. An infrared Study of the Metal-Nitrogen Band in Glycine Chelates", was prepared for publication and is now in press.

For DL-alanine, alpha-amino-isobutyric acid, and DL-isovaline studies similar to those of the glycine chelates are in progress.

2. STRUCTURE OF METAL COMPLEXES OF DIBASIC AMINO ACIDS

Bro. Columba Curran/Rev. Joseph L. Walter/R. J. Hooper 12/16/63

The infrared spectra of the dibasic amino acids, L-aspartic acid and L-glutamic acid, and their metal chelates with Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) have been obtained in the region 4000 to 270 cm^{-1}. The observed absorption bands are being assigned throughout the frequency range cited. Assignments are based on a comparison of the spectra with those of the N-deuterated amino acids and metal compleses and with the spectra of some thoroughly studied simple compounds.

An approximate normal coordinate analysis of the chelate rings in the metal complexes will be carried out in order to determine the structures of the complexes and the relative strengths of the metal-nitrogen interactions. The analysis will be performed as a seven-body problem using a valence force potential field. The resulting bond-stretching force constants will be compared with the stretching and rocking frequencies of the coordinated NH_2 groups in order to determine the validity of the use of these frequencies as a criterion for relative bond strengths in these chelates.

INFRARED ABSORPTION STUDIES (CONTD)

3. COMPLEXES OF TRANSITIONAL METAL IONS WITH DL-LEUCINE AND DL-NORVALINE

Bro. Columba Curran/Rev. J. L. Walter/J. F. Jackovitz 12/16/63

The primary object of this study is to determine the relative extent of interaction of the transition metal ions, cobalt(II), nickel(II), copper(II), platinum(II), palladium(II), zinc(II), and cadmium(II) with the amino groups of DL-leucine $((CH_3)_2CHCHNH_3^+COO^-)$ and DL-norvaline $(CH_3(CH_2)_2CHNH_3^+COO^-)$. The extent of interaction of the amino groups with the given series of metal ions will be determined through a comparison of the metal-nitrogen bond stretching force constants and the stretching and rocking frequencies of the coordinated amino groups.

All of the above chelates have been prepared, purified, and the C, H, and N analyses have been obtained. The infrared spectra have been obtained for all chelates of the DL-leucine series in the region 4000-270 cm^{-1}. Spectra for the N-deuterated chelates of the above series have also been obtained in the same region. Assignment is complete for DL-leucine and current work is concerned with assignment of the corresponding chelates and calculation of the metal-nitrogen bond stretching force constants. Work to be performed to complete this problem is repetition of the same procedure for DL-norvaline.

4. DL-PHENYLALANINE, DL-TYROSINE, AND THEIR METAL COMPLEXES

Bro. Columba Curran/Rev. Joseph L. Walter 12/16/63
Rev. Peter T. Moriwaki

Metal complexes of DL-phenylalanine with Cu(II), Ni(II), Pt(II), Pd(II), Zn(II), Co(II), Co(III) and Cr(III) have been prepared and analyzed. Infrared spectra have been recorded in the 4000 cm^{-1} to 270 cm^{-1} region. Detailed assignments for DL-phenylalanine are complete and those for the metal complexes are almost complete. The preparation of the metal complexes of DL-tyrosine is now in progress and their infrared spectra are being studied.

Future work involves the assignment of the observed absorption bands for DL-tyrosine and metal-tyrosine complexes. Calculations will be performed to determine the metal-nitrogen bond-stretching force constants for the metal complexes of both ligands by the Wilson G-F Matrix method.

SECTION 7X

NORTH AMERICAN AVIATION - ATOMICS INTERNATIONAL

7X1 High Temperature Chemistry

7X2 Radiation Chemistry

For further information on completed work, the reader is referred to the open scientific literature.

NORTH AMERICAN AVIATION Atomics International

S. J. Yosim April 15, 1964

HIGH TEMPERATURE CHEMISTRY

One of the objectives of this project is to learn enough about high temperature physical chemistry to be able to establish basic principles. The project is divided into two general areas, namely, the study of metal-metal salt systems and the study of fused salt systems.

Metal-Metal Salt Systems - The chemistry of systems of the type, metal plus metal halides, metal plus metal oxides, sulfides, etc., have been chosen for study because of the unique and interesting reactions and states of aggregation indicated by the work on these systems to date. We seek to obtain an understanding of the chemical reactions which take place, information as to the atomic, molecular and ionic species formed and thermodynamic relations descriptive of the system.

Salt Systems - The objective is to achieve an understanding of ionic substance (halides, oxides, oxy-salts, and glass systems). The basic questions of interest are those concerned with:

a) Establishing the nature of the species existing in ionic melts.
b) Determining the physico-chemical interactions between species.

Statistical mechanical studies on the theory of liquids have been fruitful, and emphasis in this area will continue. The scaled particle theory will be applied to liquid solutions, dense gases, and to additional properties of pure liquids.

Emphasis on the effects of pressure on the physico-chemical properties of high temperature melts will continue. Conductivities of pure salts and metal-salt solutions will be measured at constant volume. The importance of such measurements is that it will no longer be necessary to vary both density and temperature simultaneously. The results of these studies will help explain the maximum in the conductivity of many salts when the temperature is raised; they will also provide more evidence on the conductivity mechanism of metal-salt solutions. The effect of pressure on the metal-metal salt phase diagrams will be studied. The systems to be first investigated are $Bi-BiBr_3$ and $Bi-BiI_3$.

Electrical conductivities of additional pure salts will be measured as a function of temperature to see how prevalent the maxima in conductivities are. Some of the salts to be investigated are InI_3, ZnX_2, $CdCl_2$, $CdBr_2$, and TlX. In addition the conductivities of salts will be measured at temperatures above the critical temperature to see how ionic such systems are. These studies will begin with salts with expected low critical temperatures such as the bismuth halides. It is expected that the conductivity studies of the mixed halides will be completed.

A study of the Soret effect as well as the Seebeck coefficient will be carried out on the Bi-$BiBr_3$ system. The results of these studies will give additional evidence on the nature of the transport process as well as on the structure of the melt surrounding the diffusing species.

Publications

1. Grantham and Yosim, "Electrical Conductivities of Molten Bi-BiI_3 Solutions," J. Chem. Phys., 38 1671 (1963).

2. Topol and Ransom, "Magnetic Susceptibilities of Molten Bi-BiI_3 Solutions," J. Chem. Phys., 38, 1663 (1963).

3. Owens, "Melting Properties of Silver Nitrate to 10,000 Atmospheres," J. Chem. Phys. 39, 1053 (1963).

4. Yosim, Grantham, Luchsinger and Wilke, "Electrodeless Determination of Electrical Conductivities of Melts at Elevated Temperatures," Rev. Sci. Inst., 34, 994 (1963).

5. Yosim and Owens, "Calculation of Heats of Vaproization and Fusion of Non-Ionic Liquids from the Rigid Sphere Equation of State," J. Chem. Phys., 39, 2222 (1963).

6. Blander and Yosim, "Ionic Conformal Solution," J. Chem. Phys., 39, 2610 (1963).

7. Topol, "E.M.F. Measurements in Molten Divalent Metal-Metal Halide Solution," J. Phys. Chem. 67, 2222 (1963).

8. Grantham and Yosim, "Anomalous Behavior of the Electrical Conductivity of Molten Bismuth Halides," J. Phys. Chem., 67, 2506 (1963).

NORTH AMERICAN AVIATION Atomics International

R. B. Ingalls April 15, 1964

RADIATION CHEMISTRY

The objectives of this project are to study the fundamental processes of radiolysis of organic systems and to study in separate experiments the elementary chemical reactions postulated to occur in these systems. Of particular interest is an understanding of those processes, following the interaction of ionizing radiation, which lead to free radicals and hydrogen atoms. Thus, studies involved in characterizing and measuring yields of free radicals formed on various model organic systems during radiolysis are extremely valuable. Also, it is important that our knowledge of the reactions of hydrogen atoms including measurements of absolute reaction rates be extended. It is anticipated that the recently developed techniques for detecting radicals utilizing carbon-14 labeled methyl and ethyl radicals as radical scavengers will be useful in these studies.

The primary products of energy transfer from excited rare gases are also under investigation in order to establish by direct observation the chemical effects of energy transfer. Knowledge of the relative rate constants for these processes and their relative importance in radiation chemistry is also required.

Other means of investigating the mechanisms of organic radiation chemistry will be employed such as the isolation of particular reactions in radiolysis by the use of radioactively labeled solutes. Knowledge about certain elementary reactions of postulated free radical intermediates, for example, can frequently be obtained more readily from photochemical studies.

Four primary studies will be undertaken during the next year:

a) Refinement of Thermal Spike Model of Low LET Radiolysis of organic systems and extension to high temperature radiolysis of aliphatic systems.

b) The absolute rate constants of the reaction of hydrogen atoms with aromatic rings will be measured.

c) The absolute rate constant of the abstraction of hydrogen atoms from the alkyl groups of alkyl aromatic molecules by hydrogen atoms will be measured.

d) The yields of free radicals during radiolysis of several organic systems will be measured by the Holroyd labeled radical scavenger technique.

RADIATION CHEMISTRY

(continued)

It has been shown that the C^{14}-labeled radical scavenger can be used to detect and measure the yields of individual radicals in both saturated and unsaturated hydrocarbons. The labeled methyl radicals sample the steady-state concentration of radical intermediates forming identifiable labeled derivatives under conditions where either high dose rates or low temperatures are employed. This technique shows promise of wide application and will be particularly useful both in systems in which radiolysis leads to such a variety of products that complete product analysis is precluded and in systems consisting of very reactive organic substances where conventional radical scavengers cannot be employed. It is anticipated that yields of hydrogen atoms from hydrocarbons can also be obtained by the addition of a second additive, ethylene, a known hydrogen atom trap. The yield of ethyl radicals produced by hydrogen atom addition to the ethylene is a direct measure of the hydrogen atom yield.

In addition the study of the elementary reactions of hydrogen atoms and other free radicals with polymer fluffs will continue and will be extended to new systems.

Publications

1. Scarborough and Burr, "The Effect of Solid-Liquid Phase Transition Upon Hydrogen Yield from Biphenyl", Journal of Chemical Physics, 37, 1890 (1962).

2. M. Cher, "The Reaction of Methyl Radicals with Methanol, "Journal of Physical Chemistry, 67, 605 (1963).

3. Young, "Calculation and Display of Absorption and Derivative Curves of Gaussian and Lorentzian Functions", Journal Applied Physics, 35, 460 (1963).

4. Yang and Ingalls, "Tritium B-Decay Induced Reactions in the Polystyrene Fluff," Journal of the American Chemical Society, 85, 3920 (1963).

SECTION 8A

OAK RIDGE NATIONAL LABORATORY - CHEMISTRY DIVISION

8A1 Chemistry of the Actinide Elements

8A2 Nuclear Reaction Studies of Heavy Nuclei

8A3 Nuclear Chemistry Studies of Fission

8A4 Beta-Ray Polarization Measurements

8A5 Characterization of Low-Energy Properties of Nuclei

8A6 Development of Data Handling Systems for Nuclear Chemistry

8A7 Nuclear Chemistry - Neutron Cross Sections

8A8 Nuclear Spectroscopy

8A9 Nuclear and Inorganic Chemistry of Technetium

8A10 Paramagnetic Resonance Spectroscopy

8A11 Thermochemistry and Calorimetry

8A12 Chemistry of Aqueous Solutions: Complex Solute Species and Thermodynamics

8A13 Thermodynamic Studies of Aqueous Electrolyte Solutions over Wide Temperature Ranges

8A14 Physical Chemistry of Ion Exchangers

8A15 Development of an Ion Exchange Separation Scheme

8A16 Ion Exchange Properties of Passive Metals

8A17 Effect of Adsorbed Ions on the Electrochemical Behavior of the Active Iron Electrode

8A18 Electrochemistry of Zirconium in Hydrofluoric Acid Solutions

8A19 Solution Spectrophotometry over Wide Temperature Ranges

8A20 Molecular Beam Studies of Alkali Atom Reactions

8A

SECTION 8A Continued

8A21	Modulated Molecular Beam Studies Using Mass Spectrometric Detection
8A22	Mass Spectrometry
8A23	Comparative Inorganic Chemistry - Adsorption of Inorganic Materials
8A24	Diffraction Studies of Liquid Structure
8A25	Metal-Molten Salt Solutions
8A26	Spectroscopy of Isotopic Molecules
8A27	Chemistry of Isotopic Reactions
8A28	The Isotope Effect
8A29	Assignment of Configuration to Diastereoisomers of Glycols
8A30	The Nature of the Ionic Intermediates in Aliphatic Deamination and Related Reactions
8A31	Organic Compounds: Reactions with HNO_3 and Structural Effects on Separation of Electrolytes from Aqueous Solutions
8A32	Radiation and Hot-Atom Chemistry of Inorganic Crystalline Solids
8A33	Radiation Chemistry of Water and Aqueous Solutions
8A34	Radiation Chemistry - Studies of Energy Transfer, Charge Transfer, and Other Processes in Gas, Liquid and Solid Systems
8A35	Neutron Diffraction Crystallography

For further information on completed work, the reader is referred to the Oak Ridge National Laboratory Chemistry Division Annual progress report for the period ending June 30, 1963, ORNL-3488 and also to the open scientific literature.

OAK RIDGE NATIONAL LABORATORY Chemistry Division

A. Chetham-Strode/O. L. Keller, Jr. 11/1/63

CHEMISTRY OF THE ACTINIDE ELEMENTS

This program includes the synthesis and structural investigation of compounds and complexes of the actinide and chemically related elements. Infrared, Raman, and diffraction data on crystals are correlated with Raman spectra of solutions to determine the nature and structure of ionic species in solution. These results provide a basis for the interpretation of ionic equilibria and bonding phenomena and for the descriptive inorganic chemistry of the heaviest elements.

The program this year will emphasize the Raman spectroscopy of hydrofluoric acid solutions of protactinium and tantalum salts and the synthesis of complex protactinium fluorides. The occurrence of hydrolytic species will be studied by ultraviolet absorption spectroscopy of oxyfluoride complexes in solution.

Theoretic studies of ligand field effects in the intra-series comparative chemistry of the rare earths and actinide elements will be continued in the hope of providing an indication of the importance of these effects in ionic equilibria in solution.

Publication

1. Keller, "Identification of Complex Ions of Niobium(V) in Hydrofluoric Acid Solutions by Raman and Infrared Spectroscopy," Inorg. Chem., 2, 783 (1963).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

A Chetham-Strode/R. J. Silva 11/1/63

NUCLEAR REACTION STUDIES OF HEAVY NUCLEI

Recent advances in accelerator technology and particle detection have made it possible to extend precision nuclear reaction methods to the study of level structures in the heaviest nuclei. Reaction methods provide high resolution over a wide range of excitation energy and, additionally, are applicable to nuclei not accessible to decay scheme investigation. This program includes the study of heavy nuclei by stripping and scattering reactions and the development of the required accelerator and particle detection techniques.

Development and application of compensated silicon semiconductor detectors for the spectroscopy of 10 to 15 Mev protons will be continued. A new amplifier system will be installed with sufficient resolution and stability to allow the study of closely spaced levels in uranium and thorium isotopes. The observed levels will be characterized by angular distribution and coincidence measurements. These results will be supplemented by studies of level structures in medium weight elements of interest in connection with nuclear models.

Publications

1. Dickens, Perey, Silva and Tamura, "Proton Excitation of Two-phonon Levels," Phys. Letters, 6, 53 (1963).

2. Perey, Silva and Satchler, "Excited-core Model of Odd-A Nuclei and the Cu^{63} (p,p') Reactions," Phys. Letters, 4, 25 (1963).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

G. D. O'Kelley/E. Eichler/N. R. Johnson 11/1/63

NUCLEAR CHEMISTRY STUDIES OF FISSION

A need exists for more accurate values of cumulative and independent fission yields for thermal-neutron fission of heavy nuclei. Information concerning the division of nuclear charge in fission is essential to studies of the fission mechanism. The needed data on the distribution of primary fission yield with nuclear charge (the "charge distribution") can be obtained radiometrically by measuring the cumulative yields of early members of fission-product chains and the independent yields of later members. Detailed measurements of the variations in fission yield with changes in excitation energy are also important for an understanding of the mechanism of fission.

Recent accomplishments in this program include new information on yields and half-lives in the mass-99 fission-product chain and the independent yield of Sb^{127}, all for thermal-neutron induced fission of U^{235}. A recent determination was made of the independent yield of Nb^{97} in the fission of U^{235} by epi-cadmium neutrons.

Plans for the immediate future include measurements of cumulative yields of nuclei in the valley of the fission-yield curve of thermal-neutron induced fission. Since the charge distribution data have been more completely determined for nuclei in the heavy-mass peak of the $U^{235}(n_{th},f)$ yield curve, complementary data are needed for nuclei in the light-mass peak. Experiments will also be made to study the feasibility of performing radiochemical fission-yield determinations on spontaneous fission sources, and for neutron-induced fission at resonances in the fission cross section. Efforts to develop new experimental methods for measurements of fission yields will be continued.

Publication

1. Troutner, Ferguson, and O'Kelley, "Yields and Half-Lives in the Mass-99 Fission-Product Chain", Phys. Rev., 130, 1466 (1963).

OAK RIDGE NATIONAL LABORATORY Chemistry and Physics Division

A.R. Brosi/B.H. Ketelle/H.B. Willard 11/1/63

BETA-RAY POLARIZATION MEASUREMENTS

In this program it is planned to measure the polarization of the electrons emitted by several different nuclides which undergo beta decay. Measurements of beta-ray polarization have, in general, been consistent with the V-A theory of beta decay. A measurement of the polarization of P^{32} beta rays which was made as part of this program agreed with theory to within about 1%.

However, in several cases other workers have found discrepancies which were several times their experimental errors. It is proposed to repeat measurements in some of the cases where discrepancies exist, as well as to measure polarizations of beta rays which have not been measured previously.

Measurements will be made by the method of Mott scattering where the electron spin is rotated from longitudinal to transverse by a spherical electrostatic analyzer. The transverse polarization is then determined by a measurement of the asymmetry of electron single scattering from a gold target using semiconductors which have good energy resolution as detectors.

With further refinements in electron polarization measurements it may be possible to learn something about the nuclear matrix elements in beta decay. It may also be possible to detect or put lower limits on the amount of the pseudoscalar interaction.

Publication

1. Brosi, Galonsky, Ketelle and Willard, "A Precision Measurement of the Longitudinal Polarization of Betas Following P^{32} Decay," Nucl. Phys., 33, 353 (1962).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

G. D. O'Kelley 11/1/63

CHARACTERIZATION OF LOW-ENERGY PROPERTIES OF NUCLEI

A critical study of current nuclear theories requires detailed knowledge of nuclear energy levels, but in many cases the necessary data are lacking. Hence, the need exists for systematic studies of nuclear level schemes over a series of isotopes of an element. Most of the work on this program has been concentrated on the medium-weight nuclei, for which no truly satisfactory model applies. A continuing effort will also be carried out on deformed nuclei, where the emphasis will be on characterization of high-energy collective states and on the effects of K-band mixing.

Spectroscopy of the radiations emitted in radioactive decay is one of the most useful methods available for these studies of nuclear energy levels. Although in this work it has proved necessary to investigate radioactive nuclei over a broad half-life range, an especially large body of new data has been obtained on the short-lived fission products. These latter species, which are neutron-rich and hence possess high decay energies, excite many nuclear levels in their decay.

In addition to investigations of fission products, studies of decay schemes and gamma-gamma angular correlations were recently performed on Ne^{23} and V^{51}. An investigation was also carried out on the high-energy states of O^{17} populated in the decay of N^{17}, a delayed-neutron emitter. Future work will extend the investigation of delayed-neutron emission to the fission-product region. With new coincidence scintillation spectrometry methods, studies of medium-weight nuclei will continue, with particular emphasis on nuclei at or near the closed shells of 50 and 82 neutrons.

Publications

1. Eichler, O'Kelley, Robinson, Marinsky, and Johnson, "Nuclear Levels of Ge^{74}", Nuclear Physics, 35, 625 (1962).

2. Johnson, "Decay of Re^{184} and the Level Scheme in W^{184}", Phys. Rev., 129, 1737 (1963).

3. Robinson, Johnson and O'Kelley, "Gamma'Gamma Angular Correlation in V^{51}," Nuclear Phys. (in press).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

G. D. O'Kelley 11/1/63

DEVELOPMENT OF DATA HANDLING SYSTEMS FOR NUCLEAR CHEMISTRY

Specifications and design criteria were formulated for a multiparameter pulse-height analyzer for use in coincidence spectroscopy of radioactive nuclei. This instrument was built by an outside contractor, tested exhaustively at ORNL, and is now in use on studies of nuclear decay schemes. The analyzer contains a ferrite-core memory of 20,000 channels, each with a storage capacity of 10^6 counts. Coincidence events are sorted according to their height (channel number), and then may be stored in a basic array of 200 x 100 channels.

Outstanding features of this instrument are its versatile, cathode-ray tube display system and its ability to transfer the contents of the 20,000-channel memory onto computer-compatible magnetic tape in only 15 sec.

The formidable problem of counting the many samples from a fission-yield study created a need for more automatic data recording and processing. An automatic beta- and gamma-ray counting system which produces its information on punched cards was built by an outside contractor to our specifications.

Since both of the new instrument systems have outputs compatible with the various Oak Ridge computers, it is possible to acquire and process information far more rapidly and with greater precision than before. During the coming year much effort will be spent on writing computer programs to take full advantage of the data gathered with these instruments.

Publication

1. Goodman, O'Kelley and Bromley, "A 20,000-Channel Pulse Height Analyzer with Two Coordinate Address," pp 197-200 in Proceedings of the Symposium on Nuclear Instruments, Harwell (ed. by J. B. Birks), Academic Press, New York (1962).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

Joseph Halperin/R. W. Stoughton 11/1/63

NUCLEAR CHEMISTRY - NEUTRON CROSS SECTIONS

The quantitative estimation of neutron reaction rates in nuclear reactors is of continuing interest in nuclear research. The calculation of nuclide yields in reactor neutron spectra, evaluation of neutron fluxes and their energy dependence, and the effect of nuclide production on reactor reactivity ("neutron poison" effects) are particular examples of such interest(1, 2). Cross section measurements of neutron induced reactions (eg., (n,γ), $(n,2n)$, (n,α), (n, fission)) using primarily radiochemical and mass spectrographic techniques, and the associated problems of flux spectra determination are the major concern of this research. In particular, the measurement of thermal cross sections and resonance integrals usually provides the basis for an adequate description of reaction rates. Generally the unstable nuclides, which cannot be simply measured by transmission methods, can be most usefully analyzed by these activation techniques.

It is of interest to apply these methods to measurements with monenergetic neutrons. In this connection a crystal monochrometer is presently being assembled for studies in the thermal and near thermal energy region.

Publications

1. Stoughton and Halperin, "Effective Cutoff Energies for Boron, Cadmium, Gadolinium and Samarium Filters," Nuclear Sci. & Eng., 15, 314 (1963).

2. Halperin, et. al., "The Average Capture/Fission Ratio of U^{233} for Epithermal Neutrons," Nucl. Sci. & Eng., 16, 245 (1963).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

A. R. Brosi/B. H. Ketelle 11/1/63

NUCLEAR SPECTROSCOPY

Recent work on this program has been concerned with the decay schemes of Pr^{135} and Ce^{135}. An isomeric transition has been discovered in Ce^{135}. This is not a simple M-4 transition as is the case with the transitions from the isomeric levels in Ce^{137} and Ce^{139}.

In this work it is hoped that energy level diagrams can be worked out for both Ce^{135} and La^{135} and that spin and parity assignments can be made for at least some of the levels. It has been proposed that the isotopes in the region near the low mass number cerium isotopes have deformed nuclei which should have energy level spacings predicted by the unified nuclear model. It will be interesting to learn whether the level diagrams of the mass-135 isotopes show evidence of nuclear deformation.

In this work it is planned to use semiconductor detector spectrometers as well as scintillation spectrometers. An effort will be made to assign spins and parities to some of the levels by conversion electron angular correlation measurements.

OAK RIDGE NATIONAL LABORATORY

CHEMISTRY AND ANALYTICAL
CHEMISTRY DIVISION

G. E. Boyd/R. H. Busey/J. C. White/ D. E. LaValle

NUCLEAR AND INORGANIC CHEMISTRY OF TECHNETIUM

The purpose of this project is to obtain an improved understanding of the nuclear and inorganic chemistry of the element technetium. More complete information on the nuclear chemistry of technetium is desirable to better establish the nuclear systematics of its isotopes. The decay of the short-lived heavy Tc isotopes currently is of special interest because of recent reports of the existence of an unexpectedly long half-life at mass 104. A confirmation of the 18m Tc^{104} will be attempted by 14 Mev neutron bombardment of ruthenium enriched in Ru^{104}. Rapid chemical separations of Tc from Ru and from the uranium fission products are being developed to prepare sources of short-lived Tc^{102}, Tc^{103} and Tc^{104} for the detailed characterization of their decay schemes.

The chemistry of gram quantities of technetium (with Tc^{99g}) and its compounds is being investigated to test the predictions of the Periodic Table on the comparative chemical behavior of the Group VII B elements and to add to available information on the chemical behavior of the 4d transition elements. Thermodynamic properties of the more important compounds of technetium are being determined, and methods for the preparation of all of the oxidation states either in solid compounds or in aqueous solution are being developed. Some of the compounds will be characterized by x-ray diffraction, optical absorption and magnetic susceptibility measurements. The analytical chemistry of the element is being studied and methods for the determination of its numerous oxidation states are being devised.

Publications

1. Miller and Zittel, "Spectrophotometric Determination of Technetium with 1,5 Diphenylcarbon hydrazide", Anal. Chem., 35, 299 (1963).

2. Terry and Zittel, "Determination of Technetium by Controlled Potential Coulometric Titration in Buffered Sodium Tripolyphosphate Medium", Anal. Chem., 35, 614 (1963).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

Ralph Livingston 11/1/63

PARAMAGNETIC RESONANCE SPECTROSCOPY

The spectra arising from paramagnetic species formed by irradiating pure substances are being studied in order to identify and elucidate their properties. In the systems being studied these species are most often chemical free radicals; frequently these radicals play a direct role in the gross chemical changes ultimately brought about by the radiation. Low temperatures are usually used to stably trap the radicals during the time of study. Systems containing hydrogen and oxygen have been of particular interest, and work is under way on irradiated (for the present UV photolyzed) single crystals of hydrogen peroxide. Several paramagnetic species are formed including some in triplet states, and an effort will be made to deduce detailed properties of these species from first principles. The effects of gamma irradiation on single crystals of peroxide and ice will also be studied in detail. A triplet state species has also been seen in gamma irradiated single crystals of dimethylglyoxime where it now appears that free radicals have been formed in adjacent lattice sites giving rise to the triplet state. Defect pairs of this type will be studied in detail. Also typical of studies that have been made and which are continuing are the various species formed in irradiated crystals of nitrates and nitrites.

Publication

1. Zeldes and Livingston, "Paramagnetic Resonance Study of Production of NO_2^- in Irradiated KNO_3," J. Chem. Phys., 37, 3017 (1962).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

R. H. Busey 11/1/63

THERMOCHEMISTRY AND CALORIMETRY

The objective of the research of this project is the acquisition of thermodynamic properties (heat capacities, entropies, and free energy functions), the study of transitions arising from structural and magnetic changes, and the determination of heats of solution and formation for compounds of elements of the second and third transition series, with special emphasis on compounds of rhenium and technetium. Low temperature heat capacity (6^o to 330^oK) and high temperature enthalpy measurements are the primary observations made. Supplementary information is obtained from measurements of solubilities and heats of reaction which permit extension of certain thermodynamic properties of the compounds to the ions formed in solution.

Measurements will be made on K_2ReI_6 and K_2ReF_6 to determine if these compounds exhibit an unusual low temperature heat capacity similar to that observed for K_2ReCl_6 and K_2ReBr_6. These measurements will complete the observations on the series of paramagnetic compounds K_2ReX_6 and provide important information on the antiferromagnetism exhibited by these compounds.

The recent alteration of a thermochemical laboratory to provide for safe handling of several curies of technetium will permit low temperature heat capacity measurements to be made on large samples of technetium compounds. The first two compounds to be measured are $KTcO_4$ and K_2TcCl_6.

Publication

1. Busey, Dearman and Bevan, Jr., "The Heat Capacity of Potassium Hexachlorrhenate (IV) from 7 to 320^oK. Anomalies near 12, 76, 103 and 111^oK. Entropy and Free Energy Functions. Solubility and Heat of Solution of K_2ReCl_6. Entropy of the Hexachlororhenate Ion," J. Phys. Chem., 66, 82 (1962).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

James S. Johnson, Jr. 11/1/63

CHEMISTRY OF AQUEOUS SOLUTIONS: COMPLEX SOLUTE SPECIES AND THERMODYNAMICS

The predominant, though not exclusive, concern of this program is elucidation of the species formed by inorganic ions in hydrolytic reactions. The ions of most metallic elements of the middle rows of the periodic table react with water to form complex polymeric species, and to understand their aqueous solution chemistry, these reactions must be taken into account. Originally, the main technique was ultracentrifugation, and the problem of interpretation of refractive index patterns given by equilibrium distributions of ionic solutes has occupied a substantial fraction of the efforts up to the present. In recent years, weight-sensitive methods (on occasion light scattering as well as centrifugation) have been supplemented with other techniques, such as optical or Raman spectra or potentiometry (see publications below), when necessary. In addition, equilibrium ultracentrifugation has been employed for the measurement of activity coefficients of solutes in two component systems, and recently for solutions of two solutes.

In the near future, it is planned to complete work on several isopolyanion systems. Of these, Mo(VI) is essentially complete; W(VI), nearly so; and Ta(V), well along. A preliminary look at Si(IV) hydrolysis is in progress. Development of techniques for interpretation of ultracentrifugation data in terms of equilibrium constants will continue. If time permits, work on Th(IV) will be resumed. With respect to activity coefficient measurements, we are now engaged in work on the $NaCl-BaCl_2-H_2O$ system, and probably shall investigate one or more pairs of perchlorate salts; perchlorate media are of great importance in study of complexing reactions.

Publication

1. Rush and Johnson, "Hydrolysis of U(VI): Absorption Spectra of Chloride and Perchlorate Solutions," J. Phys. Chem., 67, 821 (1963).

8A13

OAK RIDGE NATIONAL LABORATORY Chemistry Division

M. H. Lietzke/R. W. Stoughton 11/1/63

THERMODYNAMIC STUDIES OF AQUEOUS ELECTROLYTE SOLUTIONS OVER WIDE TEMPERATURE RANGES

The general purpose of this project is to study the thermodynamic properties of aqueous solutions over wide ranges of concentration and temperature with emphasis on systems of interest in fluid reactors and in liquid chemical processing. In implementing this program two principal types of measurements have been made: EMF and solubility. The program of EMF measurements includes not only making thermodynamic studies of both simple and complex systems but also the development of both indicator and reference electrodes that will function properly over wide ranges of temperature and in a variety of electrolyte solutions. The solubility measurements offer a method of obtaining thermodynamic information on aqueous systems in temperature ranges that are difficult to study by more direct methods and make possible the extension of the studies to solutions for which no compatible electrodes have been developed.

Studies of the activity coefficient of DCl in D_2O medium, the application of glass electrodes to indicating concentrations of metallic cations, and the solubilities of multivalent electrolytes in aqueous electrolyte mixtures will be extended. Continued use will be made of the application of high speed computers to the above and related problems.

Publications

1. Lietzke and Stoughton, "The Second Dissociation Constant of Deuteriosulfuric Acid from 25 to 225^{o}," J. Phys. Chem. 67, 652 (1963).

2. Lietzke and Stoughton, "A Mathematical Model for the Solvent Extraction of Uranyl Nitrate and Nitric Acid," Nucl. Sci. and Eng., 16, 25-30 (1963).

8A14

OAK RIDGE NATIONAL LABORATORY Chemistry Division

G. E. Boyd/S. Lindenbaum 10/1/63

PHYSICAL CHEMISTRY OF ION EXCHANGERS

The long-range goal for this program is the achievement of a fundamental understanding of the behavior and properties of synthetic organic ion exchangers. Thermodynamic measurements are being conducted to learn what factors control the ionic selectivity shown by cation and anion exchangers when they are in equilibrium with electrolyte solutions. The rates of diffusion of ions in and through ion exchangers are being determined to evaluate the role of ion size and copolymer structure. Spectroscopic techniques (infra-red, visible and u.v. absorption) are being employed to identify ions inside ion exchangers.

Current work utilizes (1) C^{14} labelled tetra-alkyl ammonium ions for equilibrium and rate studies, (2) aqueous solution calorimeters for heat of exchange and apparent molal heat content measurements, and (3) radioactive, high molecular weight polymers for the measurement of the water content and electrolyte invasion of cross-linked cation exchangers. Ion exchanger beads, linear polyelectrolytes, "model compounds" and liquid ion exchangers are employed in the various phases of this program.

Publication

1. Lindenbaum and Boyd, "Spectrophotometric Investigations of the Extraction of Transition Metal Halo-Complex Ions by Liquid Anion Exchangers", J. Phys. Chem., 67, 1238 (1963).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

K. A. Kraus/F. Nelson 11/1/63

DEVELOPMENT OF AN ION EXCHANGE SEPARATIONS SCHEME

Broad comparative studies of the ion exchange behavior of essentially all elements are underway whose objectives are deeper understanding of the properties of inorganic ions in solution, development of new separations techniques, and hopefully development of a new separations scheme which would be simpler, more rapid than existing ones, and adaptable to macro and tracer concentrations. The supporting fundamental studies stress properties in concentrated electrolyte solutions in a variety of media with special emphasis on cation exchange techniques at high ionic strength which have been neglected in the past. From these studies information on thermodynamic properties such as activity coefficients in concentrated electrolyte solutions and complexing reactions can also be obtained.

8A16

OAK RIDGE NATIONAL LABORATORY Chemistry Division

George H. Cartledge 11/1/63

ION EXCHANGE PROPERTIES OF PASSIVE METALS

Measurements on the kinetics of adsorption and desorption reactions of inorganic corrosion inhibitors on passive metal surfaces are being carried out by use of electrochemical polarization techniques and of tracer methods. Information of this type is essential for the understanding of mechanisms of inhibitor action and of the effect of adsorbed species on the kinetics of electrochemical reactions important in corrosion. The passive film on iron and stainless steel retains chromate ions tenaciously and these ions may be slowly exchanged by other anions (SO_4^{-2}, OH^{-1}, etc.) in solution (see publication below). The kinetics of the exchange reactions are being measured by use of Cr^{51}(VI) as a tracer. The results may be interpreted in some cases by a complex mechanism based upon the assumption of an activation energy which increases linearly with the extent of the exchange reaction. Exchange reactions of chromate ions with other anions such as MoO_4^{-2} and PO_4^{-3} will be studied. Measurements of exchange kinetics at different temperatures are expected to provide values of activation energies of the exchange reactions.

Publication

1. Cartledge and Spahrbier, "Ion Exchange Properties of the Film on Passive Iron and Steel", J. Electrochem. Soc., 110, 644 (1963).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

E. J. Kelly 11/1/63

EFFECT OF ADSORBED IONS ON THE ELECTROCHEMICAL BEHAVIOR OF THE ACTIVE IRON ELECTRODE

The adsorption of organic ions and molecules from solution onto the surface of metals exerts remarkable effects on the kinetics of corrosion reactions. Comparative measurements on the polarization behavior of actively corroding iron electrodes in noninhibiting sulfate and in inhibiting benzoate solutions show that adsorption of the benzoate ion accelerates the specific rate of the hydrogen evolution reaction and greatly inhibits the specific rate of the iron corrosion reaction at the interface. Adsorption and desorption reactions of the organic anion are slow, thus permitting a detailed investigation of the effect of adsorption on the structure of the electrical double layer by both transient and steady state electrochemical methods. Results of this type are particularly useful for the comparison of predictions of theoretical models of the adsorption process and its effect on the structure of the double layer and on the kinetics of electrode processes with experimental observations. Future theoretical efforts will be devoted to the development of an adequate model for the interaction between specifically adsorbed ions and the other components of the electrical double layer at the metal-solution interface. Experimental measurements on the effect of organic cations on the corrosion reactions of iron will be carried out for comparison with the results obtained for organic anions.

OAK RIDGE NATIONAL LABORATORY Chemistry Division

R. E. Meyer 11/1/63

ELECTROCHEMISTRY OF ZIRCONIUM IN HYDROFLUORIC ACID SOLUTIONS

Studies on the kinetics of corrosion and film growth processes on zirconium and other metals are conducted to provide new data bearing on the nature and properties of passive oxide layers on refractory metals. Steady state and transient polarization curves obtained by classical and pulse techniques on zirconium during dissolution in the presence of hydrogen fluoride show that corrosion proceeds by continuous formation and dissolution of a passive oxide layer on the surface. Further information about the dissolution of zirconium in various solutions containing hydrogen fluoride is being obtained by use of a rotating disk electrode. The use of a rotating disk electrode possesses the advantage that mass transfer conditions are precisely defined in solution so that corrections for the contribution of mass transfer processes to measurable kinetics can be made. In this manner the kinetics of the fast interfacial reactions occurring on zirconium and other refractory metals in hydrogen fluoride solutions can be measured. Studies on interfacial reactions occurring on film-covered electrodes are being extended to tantalum, niobium, and possibly hafnium, with emphasis on dissolution reactions in hydrogen fluoride solutions, film formation processes, and kinetics of cathodic reactions.

Publication

1. R. E. Meyer, "The Reduction of Oxygen on Passive Zirconium," J. Electrochem. Soc., 110, 167 (1963).

8A19

OAK RIDGE NATIONAL LABORATORY Chemistry Division

R. W. Stoughton 11/1/63

SOLUTION SPECTROPHOTOMETRY OVER WIDE TEMPERATURE RANGES

The purpose of this program is to study the visible and near-visible spectra of solutions, particularly of electrolytes, over wide temperature ranges in order to elucidate general solute-solute and solute-solvent interactions. A spectrophotometer cell assembly has been constructed which allows simultaneous and automatic control of both sample and reference cells over the range of about -70 to 280°C. The applicability of aqueous HNO_3, H_2SO_4, and $HClO_4$ solutions (both protonated and deuterated) as suitable solvents in the equipment has been demonstrated, and their temperature and concentration ranges of stability have been determined.

In the near future solutions with liquid ammonia and methanol as solvents will be studied from the vicinity of their freezing points (-78 and -98°C, respectively) to above their critical temperatures (132 and 240°C, respectively). Also, the effects of electrolytes on the very sensitive near infra-red spectra of water (H_2O and D_2O) will be investigated.

OAK RIDGE NATIONAL LABORATORY Chemistry Division

S. Datz/E. H. Taylor/R. E. Minturn/M. G. Menendez 11/1/63

MOLECULAR BEAM STUDIES OF ALKALI ATOM REACTIONS

A study is being made of the scattering of alkali atoms from halogen molecules and atoms in an effort to observe large-cross-section coulomb scattering due to electron transfer at large impact parameters. For most alkali atom-halogen atom combinations, the internuclear separation at the crossing point between the ionic and homopolar potential curves far exceeds gas kinetic collision diameters. Thus, for those combinations in which the non-crossing rule is obeyed, the system should exist in an ionic state during the time that the atoms are within the crossing point distance. Since this leads to a coulomb scattering potential in this interval, the effect should be observable in both the total and differential scattering cross sections.

In some cases (e.g. Cs + Cl) the energy gap separating the ionic from the homopolar states at infinite distance is small enough that one may be able to observe chemi-ionization collisions and to determine the cross sections for these processes.

Studies are continuing on chemically reactive collisions of alkali atoms with halogen-containing molecules. In this work a new differential detection technique utilizing beam deflection by inhomogeneous magnetic fields is under investigation.

8A21

OAK RIDGE NATIONAL LABORATORY Chemistry Division

S. Datz/E. H. Taylor/G. E. Moore 11/1/63

MODULATED MOLECULAR BEAM STUDIES USING MASS SPECTROMETRIC DETECTION

The modulated molecular beam apparatus which utilizes mass-spectrometric detection is being used to study interactions of molecular beams with surfaces and to measure scattering cross sections of isotopic hydrogen mixtures.

In the surface reflection work, low temperature (77°K) beams of helium atoms and deuterium molecules are being reflected from heated metal surfaces. Because of the modulation frequency and flight path used, changes in velocity upon reflection are measurable as phase shifts in the modulated signal.

Surface reactions, such as the dehydrogenation of C_2H_6 and the decomposition of C_2H_6 into methyl radicals on heated Pt are also under study.

The same apparatus will be used to measure the collision cross section of HT and of D_2 with e.g. He or H_2. The comparative cross sections of these hydrogen molecules is of particular interest since they differ only in their rotational moments of inertia. Correlations will be made with the thermal diffusion factors for these two gases.

OAK RIDGE NATIONAL LABORATORY Chemistry Division

C. R. Baldock 10/28/63

MASS SPECTROMETRY

The work included here consists of two types of application of mass spectrometry to chemical problems.

The first is the measurement of changes in isotopic abundance as the result of neutron capture. This is the final step in the determination of neutron capture cross sections, the other steps of which are carried out by another group. The measurements are made with a two-stage mass spectrometer, since in many cases the ratio of abundances of the different masses which must be measured is a million or more, a circumstance requiring unusually clean separation of the mass peaks.

The second is the use of mass spectrometry to provide information of use in radiation chemistry and in other branches of chemical kinetics. This includes the nature of ions produced by electron impact, by alpha particles and by other means, the reactivities of these ions with neutral molecules, and the identities of radical and molecular species formed in various types of reaction. This work is also done with a special mass spectrometer, in this case one adaptable to high pressure (up to 1 torr) in the source and of high sensitivity.

Publications

1. Melton, "Ionization and Excitation Processes in Argon, Krypton, and the C_2 Hydrocarbons Produced by Various Means," J. Chem. Phys., 37, 562 (1962).

2. Martin*, Rummel* and Melton, "Higher Pressure Mass Spectrometry," Science, 138 (3537), 77 (1962).

---

*Chemistry Department, Vanderbilt University, Nashville, Tennessee

OAK RIDGE NATIONAL LABORATORY Chemistry Division

K. A. Kraus/H. O. Phillips 11/1/63

COMPARATIVE INORGANIC CHEMISTRY-ADSORPTION ON INORGANIC MATERIALS

For a number of years the ion exchange and adsorption properties of inorganic materials have been investigated at this laboratory. In the past principal emphasis has been on hydrous oxides and acid salts such as phosphates, tungstates, molybdates, antimonates, etc. These studies are to continue during the coming year with special emphasis on search for new materials, particularly those which are essentially exclusively anion exchange active. Typical examples are bismuth oxide, lanthanum oxide, and magnesium oxide. Their behavior and interaction with electrolyte solutions will be studied for a broad range of temperatures and compositions of the surrounding media. Within the last few years the studies have been broadened to include adsorptive properties and reactions of highly insoluble sulfides. These exhibit interesting and at times useful rapid exchange and metathetical reactions whose exploitation and further characterization will be an important part of next year's work.

Publication

1. Phillips and Kraus, "Absorption on Inorganic Materials. V. Reaction of Cadmium Sulfide with Cu(II), Hg(II) and Ag(I)," J. Am. Chem. Soc., 85, 486 (1963).

OAK RIDGE NATIONAL LABORATORY
Chemistry Division

M. A. Bredig/H. A. Levy
11/1/63

DIFFRACTION STUDIES OF LIQUID STRUCTURE

This problem is concerned with contributions to understanding of liquid structure from x-ray and neutron diffraction studies.

The experimental data yield a description of the environment of the atoms in the liquid under study in terms of the average distribution of atoms about a given atom. The combination of neutron and x-ray data for the same material makes possible a more detailed description than either technique alone.

The program is presently concerned with water, aqueous solutions, and molten binary salts.

In the case of water, a model of the local structure has been proposed which yields a good fit to the x-ray diffraction data. Studies of the effect of temperature and of solutes in the structure are in progress.

Publication

1. Danford and Levy, "The Structure of Water at Room Temperature," J. Am. Chem. Soc., 84, 3965 (1962).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

Max A. Bredig 11/1/63

METAL-MOLTEN SALT SOLUTIONS

Among studies of the chemistry of molten salts, the investigation of solutions of metals in their molten halides, which has been in progress for a number of years, is continuing. Of special interest are systems of the electropositive metals, i.e., the alkali, alkaline earth, and rare earth metals. These are distinguished from other metal-salt systems such as those of the transition and post-transition metals, by the occurrence of electronic conductance. While the study at this laboratory of the electrical conductance in most of the electropositive metal-salt solutions has been more or less completed in recent years, a few systems such as the yttrium-yttrium halide solutions remain to be investigated. As a result of very recent observations on $Ba-BaX_2$ systems, the question of the existence of solid subhalides containing alkaline earth metal ions in a low oxidation state such as M^+ or M_2^{2+} has gained renewed attention and is being investigated by thermal analysis, X-ray diffraction, and other suitable methods. An apparatus for the measurement of the Hall effect in certain alkali metal-molten halide systems has been constructed and will be used in attempts to gain further insight into the electronic behavior of such solutions. Studies of absorption and magnetic properties are also being considered.

Publication

1. Dworkin, Sallach, Bronstein, Bredig and Corbett, "The Electrical Conductivity of Solutions of Metals in their Molten Halides VI. Lanthanum, Cerium, Praseodymium, and Neodymium in their Molten Iodides," J. Phys. Chem., 67, 1145 (1963).

8A26

OAK RIDGE NATIONAL LABORATORY Chemistry Division

J. S. Drury/G. M. Begun 11/1/63

SPECTROSCOPY OF ISOTOPIC MOLECULES

Raman and infrared studies of isotopic molecules provide fundamental information from which force constants, molecular configurations, and isotopic equilibrium constants may be deducted. Such studies of the boron-10 and boron-11 species of $(CH_3)_2O \cdot BF_3$ and $(CH_2)_4O \cdot BF_3$ have been published.[1,2,3] Similar studies are in progress, or are planned, for (1) the molecular addition compounds of BF_3 with $C_6H_5OCH_3$ and $(CH_3)_2S$, (2) the xenon fluorides (XeF_2, XeF_4, XeF_6, $XeOF_4$), and (3) the related interhalogen compounds (BrF_5, IF_5, IF_7, ClO_2F). Nuclear magnetic resonance (NMR) examinations of these compounds will also be performed whenever such studies may be deemed useful.[4] Further NMR studies will be made of the kinetics and mechanism of boron exchange between the isotopic species of the reaction,

$$A \cdot B^{11}F_3(\ell) + B^{10}F_3(g) = A \cdot B^{10}F_3(\ell) + B^{11}F_3(g),$$

where A represents $(CH_2)_4O$, $(C_2H_5)_2S$, C_6H_5OH, $C_6H_5NO_2$, and $(C_2H_5)_3N$.

Publications

1. Begun, Fletcher and Palko, "Infrared and Raman Spectra of the Boron Trifluoride-Dimethyl Ether Complex," Spectrochim. Acta., 18, 655-65 (1962).

2. Palko, Begun and Landan, "Equilibrium Constant for Boron Isotope Exchange Between BF_3 and $BF_3 \cdot O(CH_3)_2$," J. Chem. Phys., 37, 552-55 (1962).

3. Begun and Palko, "Raman and Infrared Spectra of BF_3 Complexes with Diethyl Ether and Tetrahydrofuran, and the Isotopic Exchange of These Complexes with BF_3," J. Chem. Phys., 38, 2112 (1963).

4. Rutenberg, "Xenon Fluorides: Fluorine-19 Nuclear Magnetic Resonance Spectra," Science, 140, 994 (1963).

5. Rutenberg, Palko and Drury, "Nuclear Magnetic Resonance Studies of BF_3 Addition Compounds. I. The Exchange of BF_3 Between $(CH_3)_2O \cdot BF_3$ and $(C_2H_5)_2O \cdot BF_3$," J. Am. Chem. Soc., 85, 2702 (1963).

8A27

OAK RIDGE NATIONAL LABORATORY
Chemistry Division

J. S. Drury
11/1/63

CHEMISTRY OF ISOTOPIC REACTIONS

Equilibrium constants and kinetics of reactions which may serve as a basis for fractionating isotopes of the light elements and for performing other difficult separations are being systematically examined.

For separating alkali metals and their isotopes, ion exchange with polar, non-aqueous solvents will be further explored, since ethylenediamine gives a larger separation factor than water, although with a lower reaction rate. Exchange between an amalgam and an aqueous or organic solvent will be extended to zinc, magnesium, copper and similar metals.

Previous studies of isotopic exchange between BF_3 complexes and BF_3 have given one improved system for the separation and several promising possibilities. These will be tested further, and some systems containing selenium and tellurium will be explored.

Studies of the carbamate-CO_2 exchange, in which both carbon and oxygen isotopes are fractionated, will be continued. The possibility of thermal reflux lends impetus to such studies.

Large isotopic differences in the rates of reduction of NO_3^- and in the rates of thermal decomposition of substituted diazonium fluoborates have been observed. Since such information is meager for nitrogen in comparison with carbon and oxygen, these measurements will be elaborated and extended to other reactions.

OAK RIDGE NATIONAL LABORATORY Chemistry Division

C. J. Collins/V. F. Raaen 11/1/63

THE ISOTOPE EFFECT

Because of their importance to tracer chemistry, differences in reaction rates between isotopically substituted and unsubstituted compounds have been under study by this group for several years. A particular problem arises in determining secondary isotope effects in which the isotopic bond is not broken, for normal methods of measurement of these effects involve determining small differences between large numbers with an attendant increase in error. A new technique called the "differential method" has therefore been developed and applied for the purpose of measuring small, secondary isotope effects of both carbon-14 and deuterium during the formation of derivatives of several labeled ketones and aldehydes (see publication below). During the coming year the differential and related methods will be applied to studies of 1) possible π-complexes of hydrogen or deuterium; 2) the question of neighboring group participation and bridged ion formation by hydrogen or deuterium, and 3) the mechanisms of several oxidation reactions.

Publication

1. Raaen, Dunham, Thompson and Collins, "Steric Origin of Some Secondary Isotope Effects of Deuterium," J. Am. Chem. Soc., 85, 3497 (1963).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

C. J. Collins/B. M. Benjamin 11/1/63

ASSIGNMENT OF CONFIGURATION TO DIASTEREOISOMERS OF GLYCOLS

This project deals with the identification of diastereoisomeric pairs as *erythro*- (or *meso*- or *racemic*-) compounds. The correct assignment of configuration in such cases is usually done by: 1) physical methods - infrared spectroscopy and x-ray and electron diffraction crystallography and 2) chemical methods - use of relative reactivities, elimination and rearrangement reactions, stereospecific syntheses, and resolvability. The methods can be tedious and sometimes lead to erroneous conclusions (see for example, the discussion by J. H. Stocker, P. Sidisunthorn, B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **82**, 3913 (1960)). For the assignment of configuration to diastereoisomeric 1,2-diols, nuclear magnetic resonance spectroscopy is a useful tool. Thus we have shown that, when the spectra of the two compounds are measured at the same concentration, the hydroxylic-proton resonance of *meso*-2,3-diphenyl-2,3-butanediol appears at higher field strength than the hydroxylic-proton resonance of the racemic isomer. The effect seems to be general and depends upon the degree of intramolecular hydrogen bonding which will in turn depend upon the conformational and steric requirements of the substituent groups in the molecules.

Nuclear magnetic resonance measurements will be made on a series of diastereoisomers of known configuration and a correlation will be made between the chemical shifts of the groups, particularly the hydroxylic protons and the structure of the diols. The method will be extended to other classes of stereoisomers.

OAK RIDGE NATIONAL LABORATORY Chemistry Division

C. J. Collins/B. M. Benjamin 11/1/63

THE NATURE OF THE IONIC INTERMEDIATES IN ALIPHATIC DEAMINATION AND RELATED REACTIONS

Studies of the nature of the carbonium ion intermediates in deamination reactions have been a major effort of the organic group, and have been in progress for approximately ten years. Although much information has already been obtained, some important questions remain unanswered. These are: 1) What effect do the ion-pairs exert on the stereochemistry of the product? 2) Does the carbonium center become planar--if not, is this lack of planarity sufficient to control stereochemistry? 3) Under which conditions are the foregoing factors more important in controlling product stereochemistry than the steric condition of the planar carbonium ion itself?

The answers to these questions are being sought by combined stereochemical and isotopic techniques, the latter involving both tracer and isotope effect studies with carbon-14, deuterium and tritium. The same techniques will be applied to the chlorinolysis of certain thiolperoxides, a reaction which bears similarities to the deamination reaction.

Publication

1. Collins and Benjamin, "A Quantitative Test for a Classical Carbonium Ion Mechanism," J. Am. Chem. Soc., 85, 3519 (1963).

8A31

OAK RIDGE NATIONAL LABORATORY Chemistry Division

W. H. Baldwin/C. E. Higgins 11/1/63

ORGANIC COMPOUNDS: REACTIONS WITH HNO_3 AND STRUCTURAL EFFECTS ON SEPARATION OF ELECTROLYTES FROM AQUEOUS SOLUTIONS

The solvent extraction processes now employed in many nuclear fuel processing installations are operated with organic compounds in contact with aqueous solutions containing nitric acid and nitrates. A specific problem has been encountered involving the reaction between nitric acid and the hydrocarbon diluent used with tributyl phosphate as the organic solvent. Particularly significant is the formation of an unknown material that has a high affinity for zirconium. Since the diluent is a mixture of hydrocarbons and the unknown material is formed in small amounts, it seems profitable to study model compounds that might be formed in this reaction. The first class of compounds to be examined will be hydroxamic acids, RCONHOH, that are reported to form complexes with many cations but for which few data exist. Acids containing branching in the R group will be used to obtain the most favorable solubility characteristics.

Such diverse problems as the separation of electrolytes from solutions of reactor fuels and the desalination of salt water are being studied with organic compounds. Currently, the separation of the actinides from the lanthanides is an important problem. It was observed that a highly branched amide, $C_9H_{19}C(CH_3)_2CON(CH_3)_2$, shows a dramatic selectivity for uranium over thorium. Great variations in the structure of amides, i.e., in length of chain, degree of branching, and position of branching, are available through known synthetic methods. A series of amides, $RCONR'_2$, will be synthesized to relate structures, mechanism of extraction and selectivity for actinides, lanthanides, water, and sodium chloride.

OAK RIDGE NATIONAL LABORATORY Chemistry Division

G. E. Boyd 10/1/63

RADIATION AND HOT-ATOM CHEMISTRY OF INORGANIC CRYSTALLINE SOLIDS

This program is directed toward a study of the radiation chemistry of molecular ions in crystals. The ultimate objectives are the identification of the primary radiolytic processes and the development of a mechanism for the reaction of the initial products to give the final chemical species observed on analyzing the irradiated solid.

The alkali-metal and alkaline earth halates have been chosen for these investigations and results on the radiolysis of the bromates by Co^{60} gamma rays, by nuclear reactor radiations, by Li^{6} fission recoil particles and by Br-atom recoils have been obtained. The view is taken that the behavior of the radioactive recoil bromine atoms formed by thermal neutron capture in crystalline bromates can give complementary information about the damage to the molecular environment. The physical and chemical nature of the damaged region and the manner in which this changes with subsequent physical treatment of the crystal is considered to be a central problem in the radiation and hot-atom chemistry of inorganic crystalline solids.

Publication

1. Boyd, Graham and Larson, "Recoil Reactions with High Intensity Slow Neutron Sources. IV. The Radiolysis of Crystalline Alkali-Metal Bromates with γ-Rays," J. Phys. Chem., 66, 300 (1962).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

C. J. Hochanadel/J. A. Ghormley/T. J. Sworski/P. S. Rudolph/ 3/1/64
J. F. Riley/H. A. Mahlman/J. W. Boyle/A. R. Jones/H. W. Kohn/
Tsu-Chang Hung

RADIATION CHEMISTRY OF WATER AND AQUEOUS SOLUTIONS

The mechanisms through which high energy radiations bring about chemical change are being studied. We are interested in how energy is taken up in each systems studied, what the processes of energy migration and degradation are, and in the identity, the reactivity and the yields of the various transient chemical intermediates in each system. A chemical kinetics approach is generally used to elucidate a reaction mechanism; the mechanism is inferred from experimental results involving variables such as total dose, dose rate, temperature, LET, and scavenger concentration on radiolysis.

Various scavengers and tracers (such as O^{18}) are used to study the mechanism of the radiolysis of water. To identify intermediates produced, their chemical properties are compared with the properties of known intermediates generated by means other than radiolysis. Dilute aqueous solutions are studied in order to use the solute as a scavenger or detector to study the intermediates produced in the radiolysis of water, to produce unusual valence states in elements such as Cr, As, Tl, Ag, Eu, Sm.

OAK RIDGE NATIONAL LABORATORY Chemistry Division

C. J. Hochanadel/J. A. Ghormley/T. J. Sworski/P. S. Rudolph/ 3/1/64
J. F. Riley/H. A. Mahlman/J. W. Boyle/A. R. Jones/H. W. Kohn/
Tsu-chang Hung (IAEA Fellow, 1963-64).

RADIATION CHEMISTRY - STUDIES OF ENERGY TRANSFER, CHARGE TRANSFER, AND OTHER PROCESSES IN GAS, LIQUID AND SOLID SYSTEMS

Processes such as energy partition, energy transfer, charge transfer, and energy migration are studied in several types of systems other than concentrated aqueous solutions. The formation of ozone is studied in solutions of oxygen in liquid nitrogen and in liquid argon over the entire concentration range. Energy transfer in alkali halide matrices is studied by measuring the decompostion of various energy acceptors such as KNO_3 or organic materials present in small concentration ($<$.1%). The important variables are the nature of the matrix and the acceptor, and the concentration of the acceptor. Energy transfer and charge transfer processes are also studied in gas phase reactions. Present studies are concerned with the influence of CO_2 and the rare gases on the synthesis of water from H_2 and O_2. A program will be initiated to determine the relative roles of ions and excited states in gas phase radiolysis by using an applied electric field during irradiation. The effects of crystal structure and phase on the radiolysis of nitrates and bromates, and the effect of phase in the radiolysis of methane are under study. The effect of LET on the radiolysis of nitrates, chlorates, and plastics provides information on special effects in heavy particle tracks (e.g., thermal spikes). High energy radiation is used to study heterogeneous catalysis by introducing specific defects which can be related to catalytic, adsorptive, and energy-transferring properties of the solids. In addition, radiation induced reactions of materials on oxide surfaces are studied. We expect to undertake additional photochemical studies, particularly in the vacuum ultraviolet, to provide comparisons between different modes of initiation of reaction. Also, studies of reactions of ions in the mass spectrometer will be resumed.

Publications

1. Hochanadel, "Radiation Decomposition of Sodium Chlorate; Comparison of Yields and the Post-Irradiation Annealing Behavior for Irradiation by γ-Rays and α-Particles," J. Phys. Chem., 67, 2229 (1963).

2. Rudolph, Lind and Melton, "Ionic Complexes of Xe and C_2H_2 Produced by the Radiolysis of These Gases," J. Chem. Phys., 36, 1031 (1962).

3. Kohn and Taylor, "The Effect of Ionizing Radiations on Catalytic Activity. Hydrogenation and Isotopic Exchange on Inorganic Solids," J. Catalysis, 2, 32-39 (1963).

OAK RIDGE NATIONAL LABORATORY Chemistry Division

H. A. Levy/P. A. Agron/G. M. Brown/W. R. Busing/ 3/1/64
R. D. Ellison/C. K. Johnson

NEUTRON DIFFRACTION CRYSTALLOGRAPHY

This problem encompasses the investigation of crystal structures by means of the diffraction of slow neutrons. Subjects for study are chosen for their interest in structural chemistry and for their particular susceptability to solution by the neutron technique. Thus the structures of crystals containing atoms of low atomic number, particularly hydrogen, constitute a large part of the program of study.

At present structures being studied include:

1. Potassium hydrogen chloromaleate. This is of interest as a hydrogen-bonded molecule with considerable strain. Results already obtained show an unusually short hydrogen-bond. The structure is being refined.

2. Sucrose. This is the largest molecule for which a complete, precise structure has been obtained. A few minor refinements will complete the work.

3. Lithium hydroxide monohydrate. This is interesting as an inorganic hydroxide with hydrogen bonds.

4. Citric acid monohydrate. This is a molecule of biological interest, and one in which it is planned to study optical activity by enzymatic deuterium substitution.

5. Xenon hexafluoride. This will complete the series of xenon fluorides whose structures have been determined precisely by neutron and x-ray diffraction.

6. Sodium phytate (sodium inositol hexaphosphate·38 H_2O). This is of biological interest, particularly as an example of a phosphate and as a hydrate. It is being studied by x-rays rather than by neutrons because the large amount of hydrogen is a complication in a first determination of the structure. Later work, after the heavier atoms are located, may include neutron diffraction if large enough crystals can be grown.

These studies have also contributed basic information related to the geometry of hydrogen bonds in a variety of organic and inorganic crystals; a systematic dependence of hydrogen positions on the strength of the hydrogen bonds between oxygen atoms has been disclosed. Other studies contributing to understanding of hydrogen bonds are planned.

In addition to atomic positions, these studies often yield detailed information on thermal displacements and make possible deduction of rigid body molecular motions.

SECTION 8B

OAK RIDGE NATIONAL LABORATORY - ANALYTICAL CHEMISTRY DIVISION

8B1 Nuclear Methods of Chemical Analysis

8B2 Analysis of Molten Salts by Electrochemical Methods

8B3 Instrumental Methods for Chemical Analysis

8B4 Effects of Radiation on Analytical Methods

For further information on work completed, the reader is referred to the open scientific literature and to the Oak Ridge National Laboratory Analytical Chemistry Division Annual Progress Report for the period ending November 15, 1963, Report number ORNL-3537.

OAK RIDGE NATIONAL LABORATORY Analytical Chemistry Division

J. C. White/W. S. Lyon 11/1/63

NUCLEAR METHODS OF CHEMICAL ANALYSIS

This program is concerned with the study of nuclear methods of analysis involving nuclear particles other than neutrons; it involves broad research in basic analytical radiochemistry with the primary objective of searching for new, interesting, or unusual reactions or mechanisms which may be translated into useful applications. Possibilities for analytical application of α, β, γ, X-ray and bremstraahlung radiation are to be investigated. In addition the use of charged particle reactions (p,n) (p,α) He^{+3}, etc., offers the possibility of performing selected analytical determinations which may not be feasible otherwise.

In this program investigation of these nuclear phenomena and their application to analytical procedures will be studied. Alpha and beta scattering, autoradiography, and X-ray and γ-ray absorption all offer potential in analytical chemistry. Improvements in particle counting techniques, such as liquid scintillation counting and solid state detectors, make possible more sensitive detection and, hence, more useful methods for analysis.

Recent discoveries in basic nuclear physics, such as the Mossbauer effect, will be investigated for analytical purposes. The use of alpha and beta backscattering for analysis of low Z material will be investigated. The feasibility of proton activation analysis and He^{+3} bombardment for analysis will also be studied. Application of new techniques in liquid scintillation counting and solid state detection also will be initiated.

Publications

1. R. L. Hahn and W. S. Lyon, "Internal Conversion Coefficients in the Decay of Au^{199}", Phys. Rev., 130, 306 (1963).

2. R. L. Hahn, "Chemical Effects of Isomeric Transitions: The Separation of the Isomers of Te^{127}, Te^{129}, and Te^{121}," J. Chem. Phys. 39, 3482, (1963).

OAK RIDGE NATIONAL LABORATORY Analytical Chemistry Division

J. C. White/D. L. Manning/J. M. Dale 10/1/63

ANALYSIS OF MOLTEN SALTS BY ELECTROCHEMICAL METHODS

Electrochemical methods are required to ascertain the behavior of electroactive species in molten salt systems. This program is unique in that the studies are confined primarily to molten fluoride salt mixtures which present difficulties due both to high melting temperatures (~500°C) and the corrosive properties of the melt. The immediate problem here is to devise compatible containers and electrode systems. The ultimate objective of the program is to devise techniques and apparatus applicable to direct analyses of molten fluorides.

Controlled potential voltammetry (both slow and rapid scan) and chronopotentiometry were used in a study of iron and nickel in molten LiF-NaF-KF (46.5 - 11.5 - 42 mole%) to provide basic information pertaining to the half-wave potential, limiting current constant, diffusion coefficient, reversibility of the electrode reaction and activation energy of the limiting current process. The melt is contained in a graphite cell inside a quartz jacket to maintain a vacuum or controlled atmosphere. Indicator electrodes are fabricated from platinum, silver, gold, tungsten and pyrolytic graphite; the latter has proved to be the most promising electrode material tested.

Voltammetric and chronopotentiometric data will be obtained for other electroactive constituents such as chromium, uranium and oxide ion. Preliminary experiments are also planned in an effort to develop a true reference electrode for molten fluorides. Presently the potentials are referred to a platinum quasi-reference electrode.

Publications

1. D. L. Manning, "Voltammetry of Iron in Molten LiF-NaF-KF," J. Electroanal. Chem. (in press).

2. D. L. Manning and Gleb Mamantov, "Current-Voltage Curves for Zirconium and Uranium in Molten Fluorides," J. Electroanal. Chem. (in press).

OAK RIDGE NATIONAL LABORATORY — Analytical Chemistry Division

D. J. Fisher/M. T. Kelley — 11/1/63

INSTRUMENTAL METHODS FOR CHEMICAL ANALYSIS

The objective of this program is to seek out those physical or chemical properties that might best serve the purpose of chemical analysis and to develop instrumentation and advanced instrumental techniques and theory for chemical research and analysis including continuous analyses and analyses of radioactive materials. New instruments are developed in addition to improved instruments applying established principles. Information developed in this program has appeared with acknowledgement in several textbooks and several of the instruments that were developed have been duplicated in other laboratories and by commercial manufacturers. A number of operational amplifier systems have been designed or applied in various combinations in instrumentation. Emphasis is placed on the mathematical analysis of system performance and on including test functions as part of the design procedure. For new instruments, manuals are prepared that include, in addition to operating procedures, specifications defining normal instrument performance and procedures for trouble-shooting. Work in progress includes instruments and techniques for the remotely controlled analysis of radioactive materials, controlled-potential ac polarograph and polarography, a high-sensitivity conductometric titrator, a chronopotentiometer and a voltammeter for molten salt applications, and studies of potentiostat performance. Work that is scheduled includes: design and evaluation of a new fast dc polarograph, a voltammeter/chronopotentiometer/coulometric stripper, and a differential polarograph; further development of the technique of derivative dc polarography; additional investigation of the sensitivity limits of dc polarography; instrumentation for and techniques of stationary electrode voltammetry and coulometry; automation of analytical procedures.

Publications

1. Maddox, Kelley and Dean, "Determination of Chloride Ion in Dilute Solutions by Cathodic Stripping Voltammetry," J. Electroanal. Chem., 4,96 (1962).

2. "Microchemical Techniques in the Analysis of Highly Radioactive Materials," Microchemical Journal Symposium Series, Vol. 2, "Proceedings, 1961 -- International Symposium on Microchemical Techniques," Nicholas D. Cheronis, Editor, Interscience Publishers, New York, 1962, pp. 939-957.

OAK RIDGE NATIONAL LABORATORY Analytical Chemistry Division

J. C. White/H. E. Zittel 11/1/63

EFFECTS OF RADIATION ON ANALYTICAL METHODS

Definitive data on the effects of alpha, beta and gamma radiation on analytical methods that are used for the analysis of highly radioactive materials are for the most part nonexistent. This situation is particularly true with respect to more recent analytical techniques such as gas chromatography and the highly refined electroanalytical methods as well as the more established colorimetric methods. The general purpose of this program is to define (1) the nature of the effect of radiation on a specific method or technique, (2) the tolerance of the method to radiation, and (3) means of preventing or curcumventing deleterious effects if possible.

Initial efforts have involved gamma radiations from a Co^{60} source. These will be continued and similar investigations extended to alpha emitting materials also. Methods and techniques are examined to ascertain what effects such radiation induces. Typical examples are studies of the effect of radiation on (1) solvent extraction reagents, (2) the stoichiometry of UO_2, (3) electrodes used in electroanalytical methods, (4) the dissolution behavior of refractory materials after exposure to high radiation and thermal flux, and (5) actinide radiations (particularly alpha radiation) on analytical procedure.

Publications

1. Zittel, "Effect of Gamma Radiation on Aqueous Solutions of EDTA," Anal. Chem., 35, 1528 (1963).

2. Zittel, "Chromium(VI)-1,5-Diphenylcarbohydrazide Reaction and Effect of Gamma Radiation On It," Anal. Chem., 35, 329 (1963).

SECTION 8C

OAK RIDGE NATIONAL LABORATORY - REACTOR CHEMISTRY DIVISION

8C1	Radiation Chemistry of Organic Materials--High Polymers
8C2	Radiolysis of Inorganic Fluorides
8C3	Surface Chemistry of Refractory Oxides in Aqueous Media
8C4	Mechanism of Aqueous and Radiation Corrosion of Zirconium Alloys
8C5	High Temperature Aqueous Chemistry--Hydrolysis of Metal Salts
8C6	High Temperature Aqueous Systems--Electrical Conductance
8C7	High Temperature Aqueous Systems--Solubility Studies
8C8	Isopiestic Studies in High Temperature Aqueous Solution Chemistry
8C9	Physical Chemistry of Molten Salts
8C10	Phase Behavior in Fluoride Systems
8C11	Physical Chemistry of Gaseous Thermodynamic Working Fluids

For further information on completed work, the reader is referred to the open scientific literature and to the Oak Ridge National Laboratory Reactor Chemistry Division Annual Progress Report for the period ending January 31, 1964, Report number ORNL-3591.

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

W. W. Parkinson 11/1/63

RADIATION CHEMISTRY OF ORGANIC MATERIALS--HIGH POLYMERS

The general objective is the development of an understanding of the changes in molecular structure which are responsible for the radiation-induced changes in physical and mechanical properties of organic polymers. Materials under study are polystyrene, polyacrylate, and various isomeric polybutadienes.

The molecular weight and distance between cross-links influence mechanical properties very strongly. These are measured by viscosities of dilute solutions or by solubility properties. Radiation-induced changes in chemical composition are correlated with the changes in physical properties. Chemical changes are determined by infrared analysis of solid polymers and by gas chromatographic analysis of the evolved gases.

During the next year the molecular weight measurements on polystyrene will be improved by utilizing light-scattering measurements. Cross-link densities will be determined by equilibrium stress measurements. Stress relaxation and creep will be measured in air and high vacuum, at high and low temperatures. The studies will be broadened to include natural and the newer synthetic rubbers.

Publication

1. Sisman, Parkinson and Bopp, Chapters 5 and 6 of Radiation Effects on Organic Materials, edited by Bolt and Carroll, Academic Press, (1963).

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

G. H. Jenks/W. T. Rainey, Jr. 11/1/63

RADIOLYSIS OF INORGANIC FLUORIDES

The detection of elemental fluorine and carbon tetrafluoride in the cover gases following in-pile irradiation of MSRE fuel salt capsules suggested that, under undetermined conditions, radiolysis of inorganic fluorides in the frozen state had occurred with a low $G(F_2)$ value. It was assumed that carbon tetrafluoride was formed by reaction of the fluorine with graphite purposely included in the capsule or with carbon compounds present in trace impurities.

A fundamental research study of this effect has very recently been initiated, with the use of "pure radiation", e.g., a Co^{60} gamma source, X-rays, and Van de Graaff electrons, for irradiation of fluorides under a variety of conditions. The primary objectives of this program have been to determine the important parameters affecting the release of fluorine from inorganic fluorides and to describe the quantitative relationships in effect during radiolysis. The following variables were considered important and are being incorporated into experimental plans: salt composition and environment, crystal size, temperature, types of radiation, dose rate, and adsorbed dose.

Fuel salt mixtures containing LiF, BeF_2, ZrF_4, ThF_4, and UF_4 (0.70, 0.23, 0.05, 0.01, and 0.01 mole fraction, respectively) have been irradiated with the three sources under somewhat different conditions.

Continued work is planned to describe further the effects of temperature, dose rate, and type of radiation. The pure component salts will be irradiated, and the results will be compared with those from the mixed salts to determine possible synergistic influences. The effects of crystallite size and particle size will be investigated in order to determine whether or not the fluorine liberation is diffusion controlled.

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

C. H. Secoy 11/1/63

SURFACE CHEMISTRY OF REFRACTORY OXIDES IN AQUEOUS MEDIA

This program has so far concerned itself with the interaction of thorium oxide with aqueous media. The aqueous media range from very low pressure, unsaturated water vapor through pure liquid water and dilute solutions of electrolytes to concentrated solutions. In addition to very thorough determination of the geometric parameters of the solids, (surface area, particle size and distribution, crystallite size and pore size and distribution) three general experimental approaches are used. These are, first, the determination of adsorption isotherms for water and for ionic species; second, calorimetric determination of differential and integral heats of adsorption for water and for ionic species; and third, a study of electrokinetic transport, including surface conductance, in water and in electrolyte solutions.

The influence of pretreatment conditions on the heat of immersion of thorium oxide in water at 25°C has been determined. The heat of immersion is complex involving both a slow and an immediate release of heat both of which are strongly dependent on the outgassing parameters. A sensitive (10^{-7} g/g) gravimetric adsorption apparatus has been constructed. It is being used to determine adsorption isotherms and to prepare samples with known amounts of preadsorbed water for heat of immersion measurements. A major effort is the design and construction of a high-temperature, high-pressure, precision adiabatic calorimeter. This instrument should be in operation within the next year.

A non-steady state, electro-osmotic method has been used to determine electrokinetic conductance and surface conductance. Surface conductances far greater than would be expected in the diffuse part of the double layer have been observed. We believe this is attributable to the mobility of chemisorbed species.

The entire program will be extended to higher temperatures and to other refractory oxides as progress permits.

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

G. H. Jenks 11/24/63

MECHANISM OF AQUEOUS AND RADIATION CORROSION OF ZIRCONIUM ALLOYS

Reactor radiations are known to increase the corrosion of Zircaloy-2 and other zirconium-base alloys in oxygenated, high-temperature aqueous UO_2SO_4 solutions and also in oxygenated dilute acid and water. Two studies having the objective of providing information which will aid in establishing the mechanism of the radiation corrosion are in progress.

One of these has the immediate goals of determining whether the primary radiation effects occur in the metal or in the oxide, and/or whether the radiation effects are manifest only when a corrosive environment is present. Preoxidized and film-free specimens are exposed to reactor radiations while in an inert environment at 100 or 300°C, and subsequently exposed to a steam-oxygen environment at 300°C. The reactivity of a specimen and the protective qualities of the oxides formed are gauged from results of measurements of the rates of weight gain in this environment and of the A.C. film impedance of the oxides formed.

The other study has the objective of providing basic information on the corrosion of Zircaloy-2 and other metals in aqueous environments in the temperature range 100 to 300°C using electrochemical methods. The general approach from an experimental point of view is to design and fabricate equipment to perform routinely those measurements familiar to the electrochemist working on electrochemical systems at room temperature and pressure. Specifically, electrochemical measurements of corrosion rates as a function of time have been performed on crystal bar zirconium and Zircaloy-2 in highly oxygenated, dilute sulfuric acid at 167°, 208°, 268°, and 295°C. The activation energies of the anodic partial process reaction (oxidation of zirconium) and of the cathodic partial process reaction (reduction of oxygen) have also been determined.

A study of the reduction kinetics of H^+, O_2, Cu^{+2}, and UO_2^{+2} at temperatures from 100° to 300°C is planned.

Publication

1. Bacarella, "Electrochemical Measurements of Corrosion Rates on Zirconium and Zircaloy-2 at Elevated Temperatures," J. Electrochem. Soc., 103, 331 (1961).

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

C. F. Baes, Jr. 11/1/63

HIGH TEMPERATURE AQUEOUS CHEMISTRY--HYDROLYSIS OF METAL SALTS

The principal objective of this program is to determine the role of hydrolytic reactions of metallic cations in the behavior of metal salt solutions at elevated temperatures. The principal method of investigation is the potentiometric determination of acidity (pH) by use of the glass electrode (to 100°C) or the hydrogen electrode (to > 200°C) as a function of solution composition. In addition, the pH dependence of metal oxide or metal hydroxide solubility is investigated. The general approach is to study the hydrolytic behavior of a selected cation at elevated temperatures and, together with its known or measured hydrolytic behavior at room temperature, to deduce therefrom the hydrolytic reactions which occur and their temperature dependence. This information should permit a better understanding of the chemical and phase behavior of a variety of high temperature aqueous systems in terms of the ionic species of the metal which, from these studies, are expected to be present in solution. To date the hydrolysis of UO_2^{2+} and Th^{4+} have been examined in the range 25-94° and 0-94°C, respectively. During the coming year investigation of Fe^{2+} hydrolysis (in the range 25-260°C), presently in progress, will be continued, and Be^{2+} hydrolysis studies will be initiated.

Publication

1. Baes, Jr. and Meyer, "Acidity Measurements at Elevated Temperatures. I. Uranium (VI) Hydrolysis at 25 and 94°," Inorg. Chem., 1, 780 (1962).

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

W. L. Marshall/A. S. Quist 11/1/63

HIGH TEMPERATURE AQUEOUS SYSTEMS--ELECTRICAL CONDUCTANCE

The extent of electrolytic dissociation of a salt dissolved in a liquid or gas can be determined by measuring the electrical conductance of a series of solutions of varying concentration. By measurement of the conductances of many different salts under similar conditions of temperature, concentration, and pressure, not only can the extent of dissociation be determined but also the types of ions which are formed and the relative velocities with which they move in an electric field. With the use of electrical conductance as a tool, the behavior of salts in water solution is being investigated at temperatures up to 800°C and at pressures up to 4000 bars. Above 374°C and 221 bars, water ceases to behave as a liquid and can only exist as a supercritical fluid which fills its container. In a study of the behavior of a sulfate salt, the electrical conductance of K_2SO_4 dissolved in H_2O was measured at temperatures from 0 to 800°C and at pressures from 1 to 4000 bars; this showed that K_2SO_4 at high temperatures and at moderately high pressures still ionized to some extent. The specific goals of this program are (1) to complete studies of the conductances of two other electrolytes, $KHSO_4$ and H_2SO_4, in aqueous media at high temperatures and pressures (2) to use these data, in addition to those on K_2SO_4, to attempt to evaluate ionization constants for the several reaction equilibria,

$$\begin{aligned} K_2SO_4 &= K^+ + KSO_4^- \\ KSO_4^- &= K^+ + SO_4^= \\ H_2SO_4 &= H^+ + HSO_4^- \\ HSO_4^- &= H^+ + SO_4^= \end{aligned}$$

over the entire range of temperature and pressure, and (3) to derive related thermodynamic values from these constants.

Publication

1. Quist, Franck*, Jolley and Marshall, "Electrical Conductance of Aqueous Solutions at High Temperature and Pressure. I. The Conductances of K_2SO_4-H_2O Solutions from 25 to 800°C and at Pressures up to 4000 Bars, J. Phys. Chem., 67, 2453 (1963)

*E. U. Franck, Institut fur Physikalische Chemie und Elektrochemie, Karlsruhe Technische Hochschule, Karlsruhe, Germany

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

W. L. Marshall 11/1/63

HIGH TEMPERATURE AQUEOUS SYSTEMS--SOLUBILITY STUDIES

The general objectives of this program are to determine solubilities of metal sulfate salts in aqueous electrolyte media at temperatures from 100 to 374°C (the critical temperature of H_2O), and to use these data to obtain solubility products and ionization constants from which other thermodynamic values can be derived. These investigations are important not only because of the experimental information obtained but also because of the potential application of the data (1) in understanding the nature of solubility in high temperature water, (2) in evaluating chemical processes, and (3) in understanding the behavior of salts of geochemical interest. The solubilities of solids in general in very high temperature water are of particular interest because of the sparsity of information that is available. By the use of apparatus previously developed in this program, the general approach is to determine the variation in solubility of a salt as a function of the concentration of an additional electrolyte. With these data the Debye-Huckel theory can be applied for extrapolation to zero ionic strength, and thermodynamic quantities, K, ΔF^o, ΔH^o, and ΔS^o, can be obtained in addition to the mean activity coefficients of the salt as a function of ionic strength. The present goals are (1) to determine the solubilities of salts such as Na_2So_4, K_2SO_4, Li_2SO_4, and $CaSO_4$ in a variety of electrolyte media at the extremes of temperature, and (2) to obtain the various thermodynamic quantities.

Publications

1. Marshall and Gill, "Aqueous Systems at High Temperature-XI. Effect of Pressure on Liquid-Liquid Immiscibility in the System UO_2SO_4-H_2O and Liquid-Supercritical Fluid Equilibria in the System UO_2SO_4-H_2SO_4-H_2O; 290-430°C, 75-330 Bars," J. Inorg. Nucl. Chem., 25, 1033-1040 (1963).

2. Marshall and Jones, "Aqueous Systems at High Temperatures-X. Liquid-Liquid Immiscibility and Critical Phenomena in the Systems UO_3-CuO-SO_3-D_2O, UO_3-NiO-SO_3-D_2O and UO_3-CuO-NiO-SO_3-D_2O, 260-410°C," J. Inorg. Nucl. Chem., 25, 1021-1031 (1963).

3. Gill and Marshall, "Glass to Metal Tube Connector for Visual Observation of the Effect of Pressure on Phase Equilibria," Rev. Sci. Instr., 34, 442 (1963).

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

B. A. Soldano/C. H. Secoy 11/1/63

ISOPIESTIC STUDIES IN HIGH TEMPERATURE AQUEOUS SOLUTION CHEMISTRY

The general aim of this program is to obtain a systematic, comprehensive assessment of aqueous electrolyte solution behavior, with special emphasis on effects that accompany variations in temperature in the 100°C to 200°C range.

The isopiestic technique used, involving the in situ weighing of representative salts all sharing a common water vapor pressure, has proven highly effective in achieving the main objectives of this program. Studies have been completed, and the results published, for temperatures from 100° to 140°C.

The specific objectives for the forthcoming year are two-fold in nature. (1) The experimental measurement of the systematics of aqueous electrolyte behavior at 160°C should be completed. (2) The appearance of unexpected, anomalous maxima in the osmotic coefficients at low molalities and elevated temperatures for certain electrolytes will be reinvestigated. If these maxima are real, currently accepted theories will require revision.

Publication

1. Soldano and Meek, "Isopiestic Vapor-pressure Measurements of Aqueous Salt Solutions at Elevated Temperatures. Part III," J. Chem. Soc., Sept. 1963 (846), 4424-4426.

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

C. F. Baes/S. Cantor 11/1/63

PHYSICAL CHEMISTRY OF MOLTEN SALTS

The purpose of this program is the determination of the basic chemical principles of molten salt behavior which define the nature, extent and rates of chemical reactions therein. The general approach includes studies of (1) equilibrium behavior by phase, cryoscopic, calorimetric, e.m.f. and vapor pressure measurements, and (2) kinetic behavior by viscosity, diffusion, and reaction rate measurements. Present specific goals are the identification of species which occur in molten salts (principally molten fluorides) and the determination of their activity coefficients, their chemical reactivity (e.g. redox behavior) and their interactions with solvent ions. Such information should provide both the basic information necessary for the desired understanding of the chemistry of this very interesting and important branch of the liquid state, and valuable chemical knowledge in support of important nuclear and non-nuclear applications of molten salts. Plans for the coming year include continued freezing point depression, e.m.f., oxide solubility, and viscosity measurements in molten fluorides. In addition, studies are in progress on the redox and disproportionation behavior of U(III) in fluorides, the equilibrium between HF-H_2O vapor and metal fluoride-oxide mixtures in molten fluorides, and the development of a stable reference electrode for e.m.f. measurements in molten fluorides.

Publications

1. Cantor and Carlton, "Freezing Point Depressions in Sodium Fluoride. II. Effect of Tetravalent Fluorides," J. Phys. Chem., 66, 2711 (1962).

2. Cantor and Ward, "Freezing Point Depressions in Sodium Fluoride. III. Effects of 3d Transition Metal Difluorides and Cadmium Fluoride," J. Phys. Chem., 67, 1868 (1963).

3. Cantor and Ward, "Freezing Point Depressions in Sodium Fluoride. IV. Effects of Trivalent Fluorides," In Press, J. Phys. Chem. (1963).

4. Mamantov and Manning, "Current-Voltage Curves for Zirconium and Uranium in Molten Fluorides," In Press, J. Electro-analytical Chem. (1963).

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

R. E. Thoma 11/1/63

PHASE BEHAVIOR IN FLUORIDE SYSTEMS

This program is intended to provide an improved understanding of the phase behavior in fluoride systems and of the crystal structure of the complex compounds in such systems. Development of fuel mixtures for molten salt reactors required detailed investigations of phase behavior in several binary, ternary, and quaternary fluoride systems. In these studies techniques were devised to permit rapid and complete evaluation of liquid-liquid, liquid-solid, and solid-solid equilibria in such systems. Precise composition-temperature relationships were established with the use of specimens obtained by annealing mixtures of known composition in a multiply compartmented container at high temperatures in a measured thermal gradient and then quenching the container. The temperatures of phase transitions were inferred from the results of petrographic and x-ray examination of the specimens in the several compartments. The data obtained suggested a simple relationship between radii of the cations and the number, stoichiometry, and structure of the complex fluorides occurring in the system. Systematic extension of the investigation and correlation of the information confirmed the suggestion and provided a basis for prediction of the occurrence and some properties of many previously unreported compounds. Subsequent examination of additional binary systems has offered confirmation of the predictions.

Studies in the near future will be directed primarily toward phase behavior in binary systems of sodium fluoride with the rare earth trifluorides and to structure determinations of the hexagonal $NaF \cdot MF_3$ and $5NaF \cdot 9MF_3$ phase shown to be common to several of the $NaF-MF_3$ systems.

Publications

1. Thoma et al., "Phase Equilibria in the System $NaF-ThF_4-UF_4$," J. Am. Ceram. Soc., 46, 37 (1963).

2. Thoma et al., "Phase Equilibria in the System $NaF-YF_3$," Inorg. Chem., 2, 1005 (1963).

3. J. H. Burns et al., "Xenon Tetrafluoride Molecule and Its Thermal Motion: A Neutron Diffraction Study," Science, 139, 1208 (1963).

OAK RIDGE NATIONAL LABORATORY Reactor Chemistry Division

A. P. Malinauskas 10/24/63

PHYSICAL CHEMISTRY OF GASEOUS THERMODYNAMIC WORKING FLUIDS

The principal objectives of this program are twofold: (1) the extension of the kinetic theory of gases to polyatomic molecules, and (2) an elucidation of intermolecular interactions. Two phenomena exhibited by gases are currently under investigation, viz., ordinary gaseous diffusion and thermal transpiration.

The diffusion program has been planned to proceed in three stages. The first phase consists of preliminary studies with a prototype two-bulb diffusion cell for use at temperatures in the range 0°C to 150°C. During the coming year, this apparatus will be employed to obtain diffusion coefficients, as a function of temperature, for the following systems: He-Ar, He-Ne, He-Xe, He-N_2, He-O_2, He-CO, and NH_3-CO. The second phase is concerned with the design, construction, and operation of a refined version of the prototype apparatus. Unlike the diffusion chamber employed in phase 1, wherein the diffusion process is terminated in order that the compositions of the chambers can be analyzed, the refined apparatus will monitor the diffusion process continuously through the utilization of radioactive tracers. Design concepts for this apparatus, particularly those involving the gating mechanism for the isolation of the two diffusion chambers, are presently being tested on the prototype. Use of the radiotracer technique will permit a wider choice of polar gases and should be amenable to the use of the halogens. It should also be possible to investigate the effects of the distribution of mass within a molecule on the diffusion process. The utility of the diffusion phenomenon for a study of intermolecular interactions can be increased if the temperature range can be extended. Such an extension will be attempted in the third phase of the program.

It has recently been suggested that thermal transpiration data can yield information regarding the rotational relaxation times of gaseous molecules. A thermal transpiration apparatus has been constructed and is currently being used to study the effect exhibited by the following systems: Ar, Xe, N_2, O_2, CO, and CO_2. The extension to other systems, a study of the approach to the steady state, and the inclusion of a concentration gradient are also under consideration.

Publications

1. Mason*, Evans III, and Watson, "Gaseous Diffusion in Porous Media. III. Thermal Transpiration," J. Chem. Phys., 38, 1808 (1963).

2. Mason*, "Molecular Relaxation Tunes from Thermal Transpiration Measurements," J. Chem. Phys., 39, 522 (1963).

---

*E. A. Mason of the University of Maryland

SECTION 8D

OAK RIDGE NATIONAL LABORATORY - CHEMICAL TECHNOLOGY DIVISION

8D1 Separations Chemistry Research

8D2 Mechanisms of Separations Processes

8D3 Metal Nitrate Extraction by Amines (Subcontract with Massachusetts Institute of Technology)

8D4 Solvent Extraction Studies

8D5 Coalescence Studies

8D6 Stacked Clone Contactor Development

8D7 The Study of the Dynamic Behavior of Packed Gas Absorption Columns (Subcontract with the University of Tennessee)

8D8 Ion Exchange Studies

8D9 Protactinium Complex and Polymer Formation in Solution

8D10 Reserves and Process Costs of Recoverable Thorium in Granitic and Other Rocks

8D11 Geologic Aspects of Thorium Recovery from Common Rocks (Subcontract with Rice University)

8D12 Uranium and Thorium Processing

8D13 Preparation and Properties of Thoria and Urania Sols and Gels

8D14 Sintering and Surface Properties of Thoria Gels (Subcontract with the University of Utah)

8D15 Spectrophotometric Studies of High Specific Alpha Solutions at High Temperatures and Pressures

8D16 Basic Fluoride Volatility Studies

For further information on completed work, the reader is referred to the open scientific literature and to the Oak Ridge National Laboratory Chemical Technology Division Annual Progress Report for the period ending May 31, 1963, Report number ORNL-3452.

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

SEPARATIONS CHEMISTRY RESEARCH

The purpose of this program is to establish new separation systems, with continuing primary emphasis on solvent extraction systems, and to study their pertinent chemistry enabling development of new separations methods. The Program is divided into three parts: (a) Descriptive Chemistry, (b) Separations Process Development, and (c) Fundamental Chemistry.

K. B. Brown/C. A. Blake/C. F. Coleman/D. J. Crouse 10/1/63
Boyd Weaver

(a) DESCRIPTIVE CHEMISTRY

The function of the descriptive chemical studies is to search out new potentially useful extractants and other separation reagents and to evaluate their properties, in order to determine applicable areas and degree of utility in radiochemical and other separations. This is the "inventive" part of a program which, since 1950, has been responsible first for wide use of solvent extraction in ore processing and subsequently for several new developments in radiochemical and other fields.

Evaluation and systematic surveys of several useful, versatile reagents and combinations (alkylphosphonic acids, amines, phenols, synergistic combinations, etc.) are well along and will continue. Search will continue for new separations reagents, including special ion exchangers. New extractants already showing promise include: amides (U, Th), cage phosphate esters (Th, Th over U), hydroxamine acids (Zr, Nb, Hf, Sr), carboxylic acids, and reagents that may replace TBP (tributyl phosphate) in existing flowsheets such as Purex, Interim-23, etc. Diluent degradation studies are showing the reasons for poor process performance, providing methods for improving the stability against nitration of commercial aliphatic diluents, and showing potential of better performance by certain aromatic diluents.

D. J. Crouse/K. B. Brown/C. F. Coleman/B. Weaver 10/1/63

(b) SEPARATIONS PROCESS DEVELOPMENT

This part of the separations chemistry program serves to develop new solvent extraction recovery and separation processes for metals and materials not heretofore so treated and to develop more economical processes than those in existence. Here, work is carried to the point that large-scale performance can be predicted. Starting in the early 1950's, extractants found in the Descriptive Chemistry part of the program were developed into processes now widely used in the uranium ore processing industry. Those and other extractants have since been developed into practicable processes of much wider application, both within various areas of the AEC programs and as a by-product in areas useful to private industry.

Developments have been completed on vanadium recovery, thorium recovery, uranium-thorium separation, technetium and neptunium recovery, alkaline earth extractions with dialkylphosphoric acids, separations of promethium and other individual rare earths with TBP, nitrate recovery by amines, regeneration of degraded solvents by alkanolamines. Continuing developments include plutonium purification from Purex 1BP, transplutonium-actinide and inter-transplutonium separations in chloride-free systems, di-sec-butyl phenylphosphonate as a process extractant, recovery of cesium and rubidium with phenols, of strontium and other alkaline earths with carboxylic acids, of beryllium with primary amines, and of sulfuric and phosphoric acids with amines. Radiochemical processes are tested at full activity level where possible. In the future new separation schemes for short cycle fuel reprocessing, and potential use of such special reprocessing liquors as concentrated H_2SO_4 and HF, will be evaluated. Separation methods for nucleic acids and other biological materials will be studied. Methods other than solvent extraction will be included.

Publications

See ORNL Reports on Special Solvent Extraction Topics: ORNL-1959, -2173, -2720, -2744, -2820, -2941, -2952, -3064, -3071, -3106, -3185, -3204, -3496.

C. F. Coleman/W. J. McDowell/J. W. Roddy 10/1/63

(c) FUNDAMENTAL CHEMISTRY

The purpose of this part of the program is to increase the knowledge of solvent extraction chemistry and to understand the mechanisms of the different solvent extractions in such a way as to improve, extend, or define the limits of their process, analytical, and physicochemical applications. While species and equilibria are now well understood in dialkylphosphoric acid extractions of many metal ions, extraction by synergistic combinations is far less completely understood, and new synergistic combinations are continually being discovered. Still greater complications in amine extraction are attributed to large variations of organic-phase activity coefficients; here considerable progress in identification of species and correlation of parameters still fails to reconcile equilibria with the Mass Action Law.

In the future, work will continue on determination of species and equilibria in dialkylphosphoric, substituted phenol, and synergistic extraction systems, on kinetics for elucidation of extraction mechanisms, on measurement of organic-phase aggregation numbers and activity coefficients important in amine and some other extraction systems, and on elucidation of the apparent anomalies in amine extraction. Various aqueous metal complex formation constants have been evaluated through extraction equilibria; this and other uses of extraction as a tool in measurement of aqueous-phase activity coefficients and formation constants will be continued and extended.

Publications

1. McDowell and Coleman, "Reagent Dependence in Sodium and Strontium Extraction by Di(2-ethylhexyl) phosphoric Acid," J. Inorg. Nucl. Chem., 25(2), 234-5 (1963).

2. Allen and McDowell, "The Thorium Sulfate Complexes from Di-n-Decylamine Sulfate Extraction Equilibria," J. Phys. Chem., 67, 1138-40 (1963).

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

Wallace Davis, Jr. 10/1/63

MECHANISMS OF SEPARATIONS PROCESSES

This program is designed to provide a quantitative description of the mechanisms of separations processes such as solvent extraction and radiation degradation of solvents. At present, a transpirational vapor pressure method is being used to obtain activities of TBP in TBP-HNO_3-H_2O and TBP-$UO_2(NO_3)_2$-H_2O two-phase solutions. This same technique is being used to determine uranyl nitrate activities in the H_2O-HNO_3-$UO_2(NO_3)_2$ system. Future work will include extension of TBP activity measurements to solutions that contain a diluent. Later, a sixth component will be added in trace concentration to correspond to a single fission product.

Publications

1. Wallace Davis, Jr., "Thermodynamics of Extraction of Nitric Acid by Tri-n-Butyl Phosphate-Hydrocarbon Diluent Solutions". I. "Distribution Studies with TBP in Amsco 125-82 at Intermediate and Low Acidities," Nucl. Sci. and Eng. 14, 159 (1962).

2. Ibid. II. "Densities, Molar Volumes, and Water Solubilities of TBP-Amsco 125-82-HNO_3-H_2O Solutions," Nucl. Sci. and Eng. 14, 169 (1962).

3. Ibid. III. "Comparison of Literature Data," Nucl. Sci. and Eng. 14, 174 (1962).

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge, Massachusetts

ORNL Subcontract 1327

E. A. Mason

10/1/63

METAL NITRATE EXTRACTION BY AMINES

This subcontract study under the ORNL Chemical Technology Division Separations Chemistry Research program serves to supplement its descriptive chemistry and process development studies of amine extraction. The primary emphasis has been on measuring the macrochemical equilibrium extraction of fission-product and corrosion-product metal nitrates from acid solutions. With correlations essentially complete on the principal elements (molybdenum, ruthenium, zirconium, niobium showed varying extractability; rare earths and stainless steel metals almost inextractable), the extractabilities of a wider range of metal nitrates are now being surveyed, as functions of amine type and organic- and aqueous-phase compositions.

Publications

1. Vaughen and Mason, "Equilibrium Extraction of Nuclear Fuels Metals by Alkyl Amines in Nitrate Systems," Trans. Am. Nucl. Soc., 5(2), 462 (1962).

2. Skavdahl and Mason, "Extraction of Nitric Acid and Nitrosylruthenium Complexes by Alkyl Amines in Nitrate Systems," Trans. Am. Nucl. Soc., 5(2), 463 (1962).

3. Skavdahl and Mason, "The Concentrations and Amine Extraction Characteristics of Nitrosylruthenium-nitrate Complexes," Trans. Am. Nucl. Soc., 5(2), 464 (1962).

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

M. E. Whatley/A. D. Ryon 10/1/63

SOLVENT EXTRACTION STUDIES

1. Correlation of Pulse Column Capacity: The purpose of the work is to correlate the existing data on the flow capacity of pulse columns with the operating variables and the physical properties of the systems. A literature search has been completed and about 1800 data points have been compiled. Computations on a high speed computer are being made with a major segment of the data pertaining to aqueous continuous operation of stainless steel sieve plate columns. It is planned to extend the calculations for the other column variables for which data are available.

2. Hydraulics of Pulse Columns: The purpose of the study is to determine the hydraulic characteristics of pulse columns having several different types of plates. The effective orifice coefficients have been calculated from pressure data for both steady and pulsed flow conditions. Solution of equations describing flow in column and the exit jackleg is under way and should be completed very soon. No further study is planned.

3. Solvent Extraction Contactor Development: The purpose is to develop an advanced contactor for small scale development or production with radiochemical systems. The present concept is a mixer-settler with positive interface control. The mixers are driven by magnetic coupling to eliminate the troublesome bearing and seal problems of conventional contactors. A six-stage plastic unit is being constructed and will be evaluated experimentally.

Publication

1. Chester and Newman, "Liquid-Liquid Interfacial Area Determination Using a Liquid Scintillator," Journal of Tennessee Academy of Science, 38 (2), 62, (April 1963).

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

C. F. Chester 10/1/63

COALESCENCE STUDIES

The purpose of this study is to develop methods for predicting coalescence rates in ionizing radiation fields. Preliminary runs have been made with the water-benzene system using Li^6 in the aqueous phase. No effect was noted from a proton radiation, but coalescence was accelerated by an alpha radiation. A preliminary mathematical model is supported by the experimental results. The apparatus and experimental technique are being improved to reduce the statistical spread of the data. Provision is made to simultaneously record (1) 1-30 cycles per minute at 10^{-6} in. amplitude of background mechanical vibration in apparatus; (2) 10^{-4}°C temperature fluctuation; (3) neutron flux; and (4) drop lifetime. The effect of variation of system, drop size, ionizing particle type, and temperature are being studied. The effect of temperature gradients and of surface active agents on the radiation effect on coalescence will be studied.

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

W. E. Whatley/W. M. Woods 10/1/63

STACKED CLONE CONTACTOR DEVELOPMENT

It is intended to provide a high performance solvent extraction contactor capable of handling feed solutions of very high specific activity at significant plant capacities. The stacked clone contactor has been developed to the point that gross holdup times are less than 5 sec. per theoretical solvent extraction stage. Each physical stage consists of a clone 1.5 in. top diameter tapering rapidly to a 1/2-in.-diam cylindrical section to the underflow port. Each stage is 5 in. in length and develops about 70% stage efficiency. The device works best at throughputs over 50% of flooding and flow ratios, aqueous/organic, in excess of 1.

The optimum design configuration for a clone stage is being ascertained. The effect of underflow chamber volume, clone length, vortex finder, and feed port sizes and certain critical dimensions are under study. The effect of physical properties of the solvents, flow rate ratios, and throughput will be quantitatively determined on the optimum clone design. Design of a stainless steel plant prototype will be undertaken. It is planned that this unit will eventually be constructed and run on a variety of solvent extraction systems.

Patent

1. U. S. Patent No. 3,052,361, M. E. Whatley and W. M. Woods, assigned to AEC, U. S. Government, filed Dec. 6, 1960, issued Sept. 4, 1962.

UNIVERSITY OF TENNESSEE
Knoxville, Tennessee

ORNL Subcontract 2153

J. W. Prados

10/1/63

THE STUDY OF THE DYNAMIC BEHAVIOR OF PACKED GAS ABSORPTION COLUMNS

The objectives of the study are the development of mathematical techniques for describing the transient behavior of packed, countercurrent gas-liquid contacting equipment, and the evaluation of these techniques by experiment. Experiments are conducted with a column constructed of 6-in.-ID Pyrex pipe, packed to a depth of 5 ft. with 1/4- and 5/8-in. ceramic Raschig rings. The system air-carbon dioxide-water was employed, and both direct-sinusoidal and pulse forcing of the incoming gas composition were used for dynamic perturbation of the absorber. Overall amplitude ratios and phase shifts were obtained for liquid flows of 0 to 220 moles/(hr)(ft^2) and gas flows of 1 to 10 moles/(hr)(ft^2). Agreement between the two perturbation techniques was good, and reproducible results from the pulse tests extended to frequencies almost twice as great as those from direct sinusoidal tests.

A digital computer program was written for calculating theoretical amplitude ratios and phase shifts as functions of the forcing frequency under the following assumptions: (1) the equilibrium relation is linear, (2) the operating line is linear, (3) both phases move through the column in slug flow. Results of this program indicate that the dynamic behavior is primarily influenced by absorption factor, number of transfer units, and time required for liquid and gas phases to traverse one transfer unit.

Continuation of this work will involve more complex mathematical models to take into account axial mixing and end effects. The experimental work will be extended to systems of higher solubility such as the air-iodine-water system.

Publication

1. Gray and Prados, "The Dynamics of a Packed Gas Absorber by Frequency Response Analysis," A. I. Ch. E. Journal, 9, 211-216 (1963).

8D8

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

Wallace Davis, Jr. 10/1/63

ION EXCHANGE STUDIES

The objectives of the program are to develop new ion-exchange processes, to determine how such processes are limited by radiation and thermal degradation of the exchangers, and to develop methods of engineering analysis for application in AEC problems. Present studies are limited to evaluation of radiation damage to ion exchange resins in flowing water. Water is passed through the resin which is contained in a 10,000 curie cobalt-60 source and the effluent is concentrated by low temperature vacuum distillation. Analyses of the products will be used to define the mechanism of radiation damage to the resin. Future areas of study include radiation stability of cation and anion resins in other common processing environments, such as nitric and sulfuric acids; rapid oxidation and other potential hazards associated with organic resins in contact with acid media; and potential uses of inorganic ion exchangers in radiochemical processing.

8D9

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

D. O. Campbell 10/1/63

PROTACTINIUM COMPLEX AND POLYMER FORMATION IN SOLUTION

The purpose of this research is to obtain basic information on protactinium chemistry, especially solution chemistry, in systems potentially applicable to chemical separations processes. The behavior of protactinium in sulfuric acid solutions has been studied by solvent extraction and ion exchange methods, and definite evidence for the reversible polymerization of protactinium has been found.

Investigations of protactinium chemistry in sulfuric acid media are continuing, with emphasis on elucidation of the polymerization reaction. Studies of solutions containing the very effective complexing ion F^- have been initiated. Physical methods, particularly infrared and Raman spectroscopy, will be applied to the study of protactinium complexes in solution, and these results will be correlated with similar studies of crystalline compounds.

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

K. B. Brown/D. J. Crouse 11/1/63

RESERVES AND PROCESS COSTS OF RECOVERABLE THORIUM IN GRANITIC AND OTHER ROCKS

The purpose of this project is to determine, in requisite degree, the cost-quantity pattern of the earth's thorium reserves and their ability to support a long-range nuclear power economy. Such information is important to reactor program planning and studies on this project were started in 1959 after a preliminary survey revealed the paucity of knowledge about thorium reserves. Granitic rocks have been emphasized as a long-range thorium source since they comprise a large fraction of the earth's crust. With a Th/U content ratio of about 5, they also constitute a large potential uranium source. Brief evaluations of bauxites, sublateric soils, and volcanic rocks have indicated these low-grade sources to be less attractive than the granites.

From studies of numerous thorium ores and thorium bearing rocks, it is now apparent that reserves are sufficient to start large thorium reactor programs with low cost ($10/lb) thorium, supply it for a long period with low to moderate cost ($10-100/lb) thorium, and extremely long periods with high cost ($100-500/lb) thorium which would be acceptable in a successful breeder reactor. It has been found that the higher-than-average grade Conway granite in New Hampshire is an especially attractive source. This single formation contains about 14,000,000 tons of thorium in the upper 600 ft., recoverable at $75/lb thorium (plus uranium), increasing known U.S. thorium reserves by two orders of magnitude. Much greater amounts are probably available at greater depths. Several million tons of thorium are probably available from the Conway at $30-40/lb.

It is expected that this project will be completed within a year's time; work to be performed includes: (1) further laboratory testing of certain granitics to refine cost estimates, (2) studies of very deep core samples of Conway and other granites obtained from the U.S. Upper Mantle Project, (3) correlation of granite mineralogy and process behavior.

RICE UNIVERSITY
Houston, Texas

John S. Adams

ORNL Subcontract 1491

10/1/63

GEOLOGIC ASPECTS OF THORIUM RECOVERY FROM COMMON ROCKS

These studies are part of a program to determine the cost-quantity pattern of the earth's thorium reserves and their ability to support a long-range nuclear power economy. Since high-grade (low cost) reserves are limited, the program has been aimed at evaluating low grade sources, particularly granitic rock which appears to be the most attractive of the low-grade materials.

In a preliminary survey, samples were collected from many large granite formations in the United States and their thorium and uranium contents were determined. These data, coupled with process studies at Oak Ridge National Laboratory, indicated that very large tonnages of thorium are recoverable from granite at a cost tolerable for a breeder-reactor system. Recent studies have concentrated on evaluation of the Conway granite formations in New Hampshire. Thorium reserves have been estimated at about 20 million tons in the outer 600 ft. of the Conway. The uranium reserve has not been accurately determined but is expected to be about one-fifth this amount.

Autoradiographic and mineral separation techniques are being employed to identify the thorium-bearing minerals in granites and to estimate quantitatively the distribution of thorium among the minerals for correlation with processing studies at Oak Ridge.

Future studies will include (1) additional evaluation of granites including deep (1000 ft.) core samples now being obtained from the United States Upper Mantle Project, (2) continued studies of soils (laterites) and placer sands to determine the relative grade and recoverability of their thorium, and (3) continuation of studies on the micromineralization of granites.

Publication

1. Adams et. al., "The Conway Granite of New Hampshire as a Major Low-Grade Thorium Resource," Proc. National Acad. Sciences, 48, 1898-1905 (1962).

OAK RIDGE NATIONAL LABORATORY — Chemical Technology Division

D. J. Crouse/K. B. Brown — 10/1/63

URANIUM AND THORIUM PROCESSING

The purpose of this program is to develop new or improved (more economical) processes for recovering uranium and thorium (and by-product metals) from ores and purifying them for reactor use. The program was started in 1948 when a serious uranium shortage seemed unavoidable. Process developments eventually covered nearly all low and high grade uranium and thorium sources including shales, phosphate rock, lignites, Western U.S.A. ores, monazites, etc. The most notable outcome was the development of solvent extraction processes for application to uranium and thorium ores which are now widely used in the metallurgical industry. The same extractants and processes have provided a basis for greatly expanded solvent extraction technology in separation chemistry. They have now been developed for various other separations including radiochemical and are used or receiving attention in most countries throughout the world.

Current studies include (1) developing inorganic ion exchange methods for removing radium from mill wastes to permit their release to the environment and (2) improving solvent extraction processes for better economy or more diversified application. Future studies will probably include the production of reactor grade uranium and thorium at the mill (rather than in present mill-refining complex) in view of potential cost savings in fuel-cycle where large production and its attendant economies are not possible or otherwise contemplated.

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

J. P. McBride 10/1/63

PREPARATION AND PROPERTIES OF THORIA AND URANIA SOLS AND GELS

The purpose of this research is to provide basic information for use in applied programs dealing with the preparation and properties of thorium and thorium-uranium oxides and carbides. Electrophoretic, rheological, infrared, small-angle x-ray scattering, and electrodialytic methods will be employed to study thoria and urania sols and gels.

Precipitation and peptization behaviors of U(IV) nitrate and formate in ammoniacal solutions have been studied. Uranium reduction to U(IV) has been carried out both by catalyzed hydrogen reduction and by electrolytic reduction. High temperature infrared spectrophotometric studies of thoria gels and studies of the sintering behavior of thoria compacts at temperatures above 900°C are under way.

During the next year the electrophoretic and rheological studies will be continued. Urania sol and gel preparation and study will be emphasized, with the objective of better understanding what factors influence sol and gel formation and the sintering and densification behavior of the gels.

UNIVERSITY OF UTAH
Salt Lake City, Utah

ORNL Subcontract 2176

M. E. Wadsworth

10/1/63

SINTERING AND SURFACE PROPERTIES OF THORIA GELS

The purpose of this research program is to determine the densification of thoria gel and to study the colloidal and surface properties of the gel itself. Current work consists of:

1. Study of shrinkage and sintering of thoria gel;
2. Electron micrographic grain growth studies of thoria gel;
3. Grain growth studies by high temperature x-ray line broadening techniques; and
4. Infrared studies of thoria gel.

Little sintering occurs in thoria gels below 850°C, but at 1000°C the sintering process is rapid. At 1000°C, 98.2% of theoretical density is reached in about 3 hours. These results have been confirmed by the grain growth studies which show very slow crystallite growth below 850°C, becoming rapid at 1000°C or higher.

Further confirmation of these results will be sought with thicker gel samples and the sintering measurements extended to systems under applied loads and controlled atmospheres. The electron micrographic studies will be extended to a variety of times and temperatures. The x-ray line broadening study will be concentrated in the temperature range of rapid grain growth, about 1000°C. Infrared studies will be concerned with characterization of the surface water in the gels, both bonded and chemisorbed. These studies will include hydrogen-deuterium exchange, dehydration-hydration isotherms and isobars, and adsorption of various other substances such as methanol, ethanol, or glycols.

OAK RIDGE NATIONAL LABORATORY — Chemical Technology Division

R. G. Wymer/R. E. Biggers — 10/1/63

SPECTROPHOTOMETRIC STUDIES OF HIGH SPECIFIC ALPHA SOLUTIONS AT HIGH TEMPERATURES AND PRESSURES

The purpose of this research is to develop and use spectrophotometric techniques for studying aqueous solutions of uranium and transuranium elements at temperatures to 330°C. A full-scale titanium high temperature spectrophotometer cell has been built and is being tested. Equipment for density measurements of solutions at temperatures to 330°C has been constructed. Equipment is in operation to compile spectrophotometric data in a form suitable for analysis by computer programs which have been developed. A loop system for measuring spectra of circulating fluids at temperatures to 150°C has been built.

Highly alpha-radioactive solutions of transuranium elements at high temperatures and pressures will be studied. Elements to be studied include Pu, Am, Cm, Bk, Cf, Es, Fm, and Pa.

Publication

1. Wymer and Krohn, "Measuring Liquid Densities at High Temperatures and Pressures," Encyclopedia of X- and Gamma Radiation, Reinhold Publishing Corp. (1963).

OAK RIDGE NATIONAL LABORATORY Chemical Technology Division

G. I. Cathers/R. L. Jolley 10/1/63

BASIC FLUORIDE VOLATILITY STUDIES

The purpose of this program is to study the chemistry associated with the Fused Salt Volatility process with particular emphasis on new applications. The current area of study is the volatilization of PuF_6 from fused salt with emphasis on establishing the equilibrium and kinetic factors involved. Evaluation of the latter is viewed as being particularly important in operating a salt-gas contactor with a continuous gas phase.

During the next year fused salt electrochemical studies will be initiated as a more fundamental approach to serious corrosion problems and for evaluating redox equilibria existing between container metals and fused salts containing fuel components and fission products.

SUBJECT INDEX

- Absorption coefficients
  - high temperature molecules, 5B5
- Absorption columns
  - axial mixing in packed, 5A60
  - dynamic behavior of gas-liquid contactors, 8D7
  - liquid-liquid and gas-liquid agitation, 5A65
  - turbulent transfer of heat, mass, and momentum in, 1B7
- Absorption spectra
  - (See Spectra (absorption))
- Absorption spectrophotometry
  - (See Spectrophotometry)
- Accelerators
  - (See Particle accelerators)
- Acetic acid
  - anhydrous, catalytic properties, 5A61
- Acetylene
  - deuterated, infrared spectroscopy, 6-8
- Acetylides
  - neutron diffraction studies, 2A74
- Acids
  - (See also specific acids by name)
  - anhydrous, catalytic properties, 5A61
  - carboxylic, molecular complexity of organo-phosphorus compounds in, 2A86
  - dicarboxylic, chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
  - effects on ion exchange resins, 8D8
  - hydroxycarboxylic, complexes with rare earths, 1A27
  - poly, oxygen bridging studies by oxygen-17 nuclear magnetic resonance, 5B6
  - polyamino polycarboxylic, chelation of transplutonium elements, 2A90
- Acrylamide
  - absorption spectra of hydrated electrons in aqueous solutions of, 2A43
  - solid-state polymerization, spectroscopic studies, 3B7
- Acrylate polymers
  - radiation chemistry, 8C1
- Actinide rare earths
  - (See Rare earths (actinides))
- Actinium
  - atomic spectra studies, 5A56
  - emission spectroscopy, 2A72
- Actinium-226
  - fission by protons, mass distribution studies, 2A18
- Actinium-227
  - decay constants, 2A21
  - fission by protons, mass distribution studies, 2A18
- Actinium-228
  - isomers, 2A7
- Activation analysis
  - development of new methods, 8B1
  - development of techniques, 2A34
  - by helium-3 nuclear reactions, 5A57
  - of high-purity materials, 1A28
  - services at BNL, 3A13
- Activity coefficients
  - comparison of cations and anions, 2A82
  - sodium, determination in potassium - sodium solutions, 2B2
- Adsorption
  - of oxygen by metal oxides, stresses produced by, 7-23
  - properties of inorganic materials, 8A23
- Aerosols
  - reactions of solids or liquids in, effects of properties of gaseous atmosphere, 5B28
- Age determination
  - nuclear chemistry techniques, 3A3
  - potassium - argon method for meteorite minerals, 3A13
- Agitation
  - in liquid-liquid and gas-liquid equipment, 5A65
- Alanine
  - complexes with transition metals, 7-39
- Alanine, phenyl-
  - metal complexes, infrared spectra, 7-39
- Alcohols
  - (See also specific alcohols by name)
  - aliphatic, solvated electron formation in radiation of, 2A41
  - dehydration, as carbonium ion prototype reaction, 3A9
  - molecular complexity of organo-phosphorus compounds in, 2A86
- Aldehydes
  - (See also specific aldehydes, e.g., Salicylaldehydes, chloro-)
  - formation, isotope effects, 8A28
- Algae
  - chlorophyll reactivity studies, 2A51
  - deuteriated, photosynthesis studies, 2A51
  - growth in heavy water, 2A50
- Aliphatic compounds
  - (See also Hydrocarbons and specific aliphatic compounds by name)
  - deamination reactions, studies of ionic intermediates, 8A30
  - deuterated, effect on pi-complex formation, 3A7
  - dialkylphosphinyl alkanes, use as solvent extractants, 1A2
  - hydrolysis, as carbonium ion prototype reaction, 3A9
  - molecular complexity of organo-phosphorus compounds in, 2A86
- Alkali metals
  - atomic beams, collisions with halogens, 8A20
  - compounds, anion effects on thermal ionization from metal filaments, 2A53
  - determination of radiative lifetime in excited state, 5B3
  - elastic scattering of crossed beams, 5B22
  - halates, radiolysis, 8A32
  - halides, color center studies in crystals, 7-22
  - halides, energy transfer in radiation chemical studies, 8A34
  - isotope separation by exchange reactions, 8A27
  - molten salt solutions, 8A25
  - solvent extraction with polyiodides, 3B5
  - uranates, uranium-oxygen bond studies, 2A78

- Alkali metals (liquid)
  - solubility of rare gases in, 2B1
- Alkali metals, alloys
  - solubility in fused salts, 2B8
- Alkali metals, alloys (liquid)
  - thermodynamic properties of binary solutions, 2B2
- Alkaline earth metals
  - coulometric titration, 1A1
  - halates, radiolysis, 8A32
  - molten salt solutions, 8A25
  - oxides, oxygen determination in, 2A36
  - separations by ion exchange, 1A5
  - solvent extraction with nitrobenzene-iodine solution, 3B5
  - uranates, uranium-oxygen bond studies, 2A78
- Alkaline earth metals, alloys
  - solubility in fused salts, 2B8
- Alkoxy groups
  - effect on extraction of rare earths by organophosphorus compounds, 2A89
  - effect on molecular complexity of organophosphorus compounds in solutions, 2A86
- Alkyl amines
  - solvent extraction studies, 4-2
- Alkyl groups
  - effect on extraction of rate earths by organophosphorus compounds, 2A89
  - effect on molecular complexity of organophosphorus compounds in solutions, 2A86
- Alkyl thiocyanates
  - spectroscopic studies of characteristic vibrations, 1A8
- Allene
  - deuterated, infrared spectroscopy, 6-8
- Allomerization
  - deuteriated chlorophyll, 2A51
- Alloys
  - (See also specific alloys by name, e.g., Iron alloys)
  - liquid, thermodynamic properties, 5A62
  - non-ferrous, fluorometric determination, 7-38
- Alpha particles
  - angular distribution of emission, studies using oriented nuclei, 5A1
  - decay calculations for deformed nuclei, 5A15
  - energy resolution by liquid scintillators, 2A26
  - high-energy reactions, 2A16
  - induction of (α,d) reactions with light nuclei, 5A28
  - inelastic scattering, angular correlation studies, 5A33
  - initiation of chemical reactions, 3B6
  - nuclear reactions by, 2A1
  - nuclear reactions at high energy, 5A32
  - platinum isotope decay studies, 5A11
  - scattering, lunar surface analysis by, 2A28
  - sources, calibrator construction, 3B6
- Aluminum chloride
  - Lewis acidity, 7-34
- Aluminum chloride (liquid)
  - coordination number of transition metal ions in, 2A63
- Aluminum halides
  - aluminum solution in, 1A20
- Aluminum intermetallic compounds ($AlCr_2$)
  - neutron diffraction studies, 2A74
- Aluminum, triphenyl-
  - structure, 1A11
- Amalgams
  - isotope exchange reactions with solutions, 8A27
- Americium
  - crystal-structure studies, 5A54
  - emission spectroscopy, 2A72
  - irradiation with helium ions and deuterons, 2A1
  - solvent extraction studies, 3B8
  - spectrophotometry of solutions at high temperatures and pressures, 8D15
- Americium-241
  - neutron fission cross sections, 2A8
- Americium-243
  - neutron cross sections, 2A8
- Americium-244
  - isomers, 2A7
- Americium-246
  - isomers, 2A7
- Americium chlorides ($AmCl_3$)
  - thermal expansion and crystal structure, 5A42
- Americium fluorides (AmF_6)
  - preparation attempt, 2A60
- Americium ions
  - electronic energy level studies, 5A52
  - solid-state spectra studies, 5A55
  - thermodynamic data, 5A53
- Americium oxides
  - preparation in fused salt solutions, 2A62
- Americium oxides (AmO_2)
  - vapor pressure, 2A60
- Amides
  - (See also specific amides by name e.g., Benzamide)
  - cyclic, barrier studies by nuclear magnetic resonance, 3A7
  - solvent extraction properties, 8A31
  - spectroscopic studies of characteristic vibrations, 1A8
- Amines
  - metal halide complexes, dissociation in solution, 7-30
  - reactions, intermediate ion studies, 8A30
  - solvent extraction of melted nitrates with, 8D3
  - solvent extraction studies, 4-2
  - solvent extraction studies, 5A50
- Amino acids
  - (See also specific amino acids by name)
  - dibasic, infrared spectra of metal complexes of, 7-39
  - radiolysis, 5A77
- Amino compounds
  - poly carboxylic acid polymers, chelation of trans-plutonium elements, 2A90
- Amino group
  - infrared spectral studies in metal complexes of dibasic amino acids, 7-39
- Aminoisobutyric acid
  - complexes with transition metals, 7-39
- Ammonia
  - conversion to hydrazine, radiation induced, 5B23
  - diffusion studies, 8C11
  - radiolysis, effects of density, 7-4
  - reactions with disulfur dichloride, 5B7
  - substitution rates in platinum complexes, 1A24
  - vacuum ultraviolet photochemistry, 7-2
- Ammonia (liquid)
  - calcium electrochemical studies in, 5B30
  - chemistry in, 5B9
  - pulse radiolysis studies, 2A44
  - solvent, spectrophotometry, 8A19
- Ammonium ions
  - tetra alkyl, ion exchange studies, 8A14
- Amplifiers
  - calibration and stabilization, 5A40
- Amplifiers (pulse)
  - design and development, 5A39
- Analog systems
  - study of liquid kinetics by fluidized glass spheres, 5A63
- Analytical chemistry
  - differential migration technique, 2A32
  - electrometric methods, 1A1

  by emission spectroscopy, 1A7
  by emission spectrography, 2A35
  instrumental methods, development, 8B3
  nuclear methods, basic research, 8B1
  radiation effects on, 8B4
  by reversed-phase chromatography, 1A4
  separations by ion exchange, 1A5
  services at BNL, 3A13
  simultaneous determination of elements in submilligram organic samples, 5A71
  uranium isotopic determination by atomic absorption spectrophotometry, 2A37
Angular momentum
  effects on fission barriers, 5A16
  fission fragments, studies of prompt gamma ray emission, 5A17
Aniline
  complexes with metal halides, dissociation in solution, 7-30
Anions
  comparison of activity coefficients with cations, 2A82
  interactions in aqueous solutions, theoretical studies, 2A81
  interaction with metal ions, spectral studies, 2A65
p-Anisidine
  complexes with metal halides, dissociation in solution, 7-30
Anisotropy
  alpha particle emission, studies using oriented nuclei, 5A1
  beta particle emission, studies using oriented nuclei, 5A1
Anthracene
  solutions in aliphatic alcohols, solvated electron studies, 2A41
Antiferromagnetism
  materials, heat capacities at low temperatures, 5B24
  transition element compounds, 8A11
Antimonates
  ion exchange and adsorption properties, 8A23
Antimony-122
  beta decay spectra, shape studies, 2A25
Antimony-127
  yield from uranium-235 fission, 8A3
Appearance potentials
  for metastable electronic states in molecules, 5A44
  for multiply charged ions in mass spectrometers, 5A45
Aqueous solutions
    (See Solutions (aqueous))
Archaeology
  analysis of artifacts at BNL, 3A13
Argon
  diffusion studies, 8C11
  reaction with free radicals, electron paramagnetic resonance studies, 5B17
  thermodynamic properties, determination from solubility in liquid alkali metals, 2B1
Argon (liquid)
  oxygen radiation chemical reactions in, 8A34
Argon-42
  production by Ar^{40}(t,p)Ar^{42} reaction, 3B10
Argon-34
  (p,t) reaction, nuclear energy level studies, 5A27
Argon - potassium dating
    (See Age determination)
Argon resonance lamps
  development, 6-3
Arochlors
  separation from water, design of liquid-liquid settler, 5A68
Aromatic compounds
    (See also Hydrocarbons and specific aromatic compounds by name)
  free-radical substitution, 7-27
  nitration in vapor phase, 5A61
  reactivity, structural studies of, 3A9
Aroxy groups
  effect on extraction of rare earths by organophosphorus compounds, 2A89
  effect on molecular complexity of organophosphorus compounds in solutions, 2A86
Arsenic
  valence state produced by radiolysis of aqueous solutions, 8A33
Artifacts
  analytical studies at BNL, 3A13
Aryl groups
  effect on extraction of rate earths by organophosphorus compounds, 2A89
  effect on molecular complexity of organophosphorus compounds in solutions, 2A86
Aspartic acid
  metal complexes, infrared spectra, 7-39
Astatine
  chemical properties, 2A59
Astatine-205
  nuclear structure, gamma ray spectra studies, 5A8
Astatine-208
  nuclear structure studies, 5A8
Astatine hydrides (AtH)
  identification, 2A59
Astatine iodides (AtI)
  production and identification, 2A59
Atomic spectra
    (See Spectra)
Atoms
  absorption spectra of rare earths, 1A8
  configuration interaction spectra, 5A43
  orbital electron interactions with nuclear transitions, 3A2
  rare earths, theoretical studies of spectra, 2A76
  reactions with molecules in crossed-beam studies, 2A39
Atomic beams
  of alkali metals, scattering in crossed, 5B22
Autoradiography
  oil paintings, analytical technique using neutron activation, 3A13
Azo compounds
  deuterated, isotopic effects on decomposition, 3A7
Azoethane
  decomposition by gamma-radiation, 3A5
Bacteria
  chlorophyll reactivity studies, 2A51
  conversion of inorganic compounds, studies on, 5A69
  growth in heavy water, 2A50
Barium
  solution in barium halides, 8A25
Barium chloride systems (BaCl$_2$-NaCl)
  hydrolytic reactions in aqueous solution, 8A12
Barium halides
  barium solution in, 8A25
Barium titanates (BaTiO$_3$)
  crystal structure, x-ray diffraction studies, 2A71
Benzamide
  spectroscopic studies of characteristic vibrations, 1A8
Benzene
  arylation, isotope effects, 7-27
  excited molecules, energy transfer studies, 7-2
  molecular complexity of organo-phosphorus compounds, in, 2A86

  - molecular complexity of organophosphorus compounds in, 2A89
  - photochemistry of, energy paths in, 2A49
  - recoil chemistry of carbon-11, 1A29
  - solutions, energy transfer in luminescence, 7-8
  - triplet state formed by radiolysis, 7-4
- Benzene-d_1
  - reaction with phenylazotriphenylmethane, isotope effects, 7-27
- Benzene, diamino-
  - reduction studies, 3B8
- Benzene, perfluoro-
  - radiation and heat effects on, 3B3
- Benzoate ions
  - corrosion inhibition by adsorption, 8A17
- 1,4-Benzoquinone, 2,5-dihydroxy-
  - chelates with di, tri-, and tetra- valent metal ions, properties of, 7-35
- Berkelium
  - emission spectroscopy, 2A72
  - spectrophotometry of solutions at high temperatures and pressures, 8D15
  - valence studies, 5A54
- Berkelium-245
  - nuclear properties, 2A7
- Berkelium-246
  - isomers, 2A7
- Berkelium-247
  - nuclear properties, 2A7
- Berkelium-248
  - nuclear properties, 2A7
- Berkelium-249
  - neutron cross sections, 2A8
  - nuclear energy levels, electron spectrometry studies, 5A4
  - nuclear properties, 2A7
  - photofission, 2A1
- Berkelium dioxide
  - crystal structure studies, 5A42
- Berkelium oxychloride
  - crystal structure studies, 5A42
- Berkelium trichloride
  - crystal structure studies, 5A42
- Beryllium
  - oxygen removal from liquid by hydrogen reduction, 5A66
- Beryllium fluoride
  - radiolysis, 8C2
- Beryllium ions
  - hydrolysis at high temperature, 8C5
- Beta decay
  - experimental studies, 2A25
  - polarization studies, 8A4
- Beta particles
  - (See also Electrons)
  - angular distribution of emission, nuclear orientation studies, 5A2
  - angular distribution of emission, studies using oriented nuclei, 5A1
  - automatic counting instrument, 8A6
  - polarization studies, 8A4
  - spectra, computer analysis, 2A24
  - spectrometry, radioactive decay studies by, 2A23
- Bicyclohexyl, perfluoro-
  - radiation and heat, effects on, 3B3
- Binding energies
  - (See also Nuclei)
  - spherical nuclei, theoretical calculation comparison with experiment, 5A15
- Biochemistry
  - enzyme reactions, low temperature studies, 3A11
  - tracer studies of learning process in planarians, 3A11
- Biosynthesis
  - deuteriated chlorophyll, 2A51
  - in organisms grown in heavy water, 2A50
- Biphenyl, perfluoro-
  - radiation and heat effects on, 3B3
- Bis (8-quinolinato) tin
  - (See Tin, bis (8-quinolinato))
- Bismuth
  - bombardment with oxygen-16 ions, fission excitation function measurements, 5A21
  - phase studies at high pressure, 5B11
- Bismuth-209
  - fission by high-energy protons, 2A9
  - fission studies with high-energy helium ions, 2A19
  - $(p, p\pi^+)$ reaction, 2A13
- Bismuth-210
  - calculations on double closed-shell core model, 5A14
- Bismuth alloys
  - solubility in fused salts, 2B8
- Bismuth alloys (Bi-Pb)
  - cadmium separation by extraction with a fused salt, 1B2
- Bismuth alloys (Bi-Li)
  - solubility in lithium chloride - lithium fluoride systems, 2B8
  - spectrophotometry in fused salt solutions, 2B8
  - thermodynamic properties, regenerative cell studies, 2B7
- Bismuth alloys (Bi-Na)
  - thermodynamic properties, regenerative cell studies, 2B7
- Bismuth bromide systems (Bi-$BiBr_3$)(liquid)
  - chemistry, 7X1
- Bismuth iodide systems (Bi-BiI_3)(liquid)
  - chemistry, 7X1
- Bismuth chlorides
  - bonding studies, 1A19
- Bismuth oxides
  - ion exchange properties, 8A23
- Bismuth systems (Bi-$BiBr_3$)(liquid)
  - chemistry, 7X1
- Bismuth systems (Bi-BiI_3)(liquid)
  - chemistry, 7X1
- Bomb calorimetry
  - (See Calorimetry)
- Bonds
  - actinides, complex ions, 4-1
  - actinide complexes, 4-3
  - actinide compounds, 8A1
  - carbon-carbon, vibrational analysis in alkyl thiocyanates, 1A8
  - carbon-sulfur, vibrational analysis in alkyl thiocyanates, 1A8
  - cesium-cesium, energy, 5B15
  - chelate compounds, strength studies, 7-39
  - covalency in lanthanide rare earths, 2A65
  - fluorine-fluorine, coupling constant studies, 5B25
  - fundamental studies, 1A11
  - high temperature studies in solids, liquids, and gases, 2A54
  - hydrogen bonds in solvent extraction, 4-2
  - hydrogen-carbon-hydrogen, angle studies, 5B25
  - hydrogen, inter- and intra-molecular types in phenol derivatives, 2A82
  - hydrogen, nature of in acidic organophosphorus compounds, 2A87
  - metal-nitrogen, stretching force constant studies, 7-39
  - Mossbauer effect in studies of, 5A48
  - phosphorus-sulfur, infrared spectra, 7-31
  - potassium-potassium, energy of, 5B15
  - rubidium-rubidium, energy of, 5B15
  - sigma, isotope effects studies, 3A7

  sodium-sodium, energy, 5B15
  study by molecular beam electric resonance spectroscopy, 5A46
  uranium-oxygen, measurements of, 2A78
  xenon hexafluoride, theoretical studies, 2A66
Boranes, t-butyldiisobutyl-
  isomerization to triisobutylborane, kinetics, 7-32
Boranes, trialkyl-
  isomerization of α-branched, kinetics and equilibria, 7-32
  unsymmetrical primary, kinetics and equilibria in redistribution reactions, 7-32
Boranes, tri-sec-butyl
  isomerization to tri-n-propylborane and tri-n-butylborane, kinetics, 7-32
Boric acid complexes
  optical rotatory dispersion studies, 2A57
Borides
    (See also specific borides by name e.g., Hafnium borides (HfB_2))
  enthalpy of formation, 2B10
Borohydride ion
  reaction with germanium hydrides, 5B8
  reduction of inorganic ions by, 5B8
Boron chlorides (BCl_3)
  Lewis acidity, 7-34
Boron fluoride complexes (BF_3-dimethylether)
  Raman and infrared spectra, isotope effects, 8A26
Boron fluoride systems ($BF_3 \cdot XeF_6$)
  complex formation in xenon fluoride studies, 2A66
Boron fluorides (BF_3)
  compressibility isotherms, determination, 6-6
  enthalpy of formation, 2B10
  isotope exchange with complexes, 8A27
  Lewis acidity, 7-34
Boron hydride ions (GeH_3BH_3)
  preparation, 5B8
Boron isotopes
  separation by isotopic exchange, 8A27
Bromates
  radiolysis, effects of crystal structure and phase, 8A34
  spectral studies, 2A87
Bromine fluorides (BrF_3)
  Raman spectroscopy of solutions using laser light source, 2A67
Bromine ions
  reaction rate with xenon trioxide in acidic solution, 5A49
4-Bromo-p-terphenyl
    (See Terphenyl, 4-bromo-p-)
Butadiene polymers
  radiation chemistry, 8C1
Butane
  photochemistry, 6-3
2-Butanone, 3-phenyl-
  reduction by lithium aluminum hydride, stereochemistry, 7-28
tri-sec-Butyl borane
    (See Boranes, tri-sec-butyl-)
t-Butyldiisobutyl borane
    (See Boranes, t-butyldiisobutyl-)
Butyl ether
  molecular complexity of organo-phosphorus compounds in, 2A86
Cadmium
  solvent extraction with a fused salt - molten metal system, 1B2
Cadmium alloys
  solubility in fused salts, 2B8
Cadmium alloys (Cd-Ce)(liquid)
  phase studies, 2B4
  thermodynamic properties, 2B3
Cadmium alloys (Cd-La)(liquid)
  phase studies, 2B4
  thermodynamic properties, 2B3
Cadmium alloys (Cd-Nd)(liquid)
  phase studies, 2B4
Cadmium alloys (Cd-Pu)(liquid)
  thermodynamic properties, 2B3
Cadmium alloys (Cd-Pr)(liquid)
  phase studies, 2B4
  thermodynamic properties, 2B3
Cadmium alloys (Cd-U)(liquid)
  thermodynamic properties, 2B3
Cadmium bromide
  chemistry of fused, 7X1
Cadmium cesium chloride
    (See Cesium cadmium chlorides ($CsCdCl_3$))
Cadmium chloride
  chemistry of fused, 7X1
Cadmium chloride systems ($CdCl_2$-KCl)
  calorimetric studies of complexes in fused, 6-10
Cadmium halides
  cadmium solution in, 1A20
  complexes with aryl amines, dissociation in solution, 7-30
Cadmium intermetallic compounds (UCd_{11})
  magnetic susceptibility, 2A83
Cadmium ions
  absorption spectra of hydrated electrons in aqueous solutions of, 2A43
  alkylhydroxy substituted pyridine complexes, formation constants, 7-33
  complexes with dibasic amino acids, infrared spectra, 7-39
  complexes with DL-leucine, infrared spectra, 7-39
  complexes with DL-norvaline, infrared spectra, 7-39
  half-wave potential and diffusion current in solutions, 7-33
Calcium
  absorption spectrum in liquid ammonia, 5B9
  electrochemical studies in liquid ammonia, 5B30
  (α,d) reaction, excitation of scandium-42 product, 5A28
Calcium-38
  (p,t) reaction, nuclear energy level studies, 5A27
Calcium-40
  (p,t) reaction, nuclear energy level studies, 5A27
  search for, 2A27
Calcium-50
  search for, 3B10
Calcium fluoride
  divalent rare earth preparation using, 2A61
Calcium sulfate
  solubility in water at high temperature, 8C7
Californium
  alpha particle emission, angular distribution studies, 5A1
  atomic spectra studies, 5A56
  bombardment with heavy ions, 5A5
  emission spectroscopy, 2A72
  oxidation in aqueous solutions, 2A60
  spectrophotometry of solutions at high temperatures and pressures, 8D15
  valence studies, 5A54
Californium-246
  nuclear properties, 2A7
Californium-248
  nuclear properties, 2A7
Californium-250

  neutron cross sections, 2A8
Californium-251
  neutron cross sections, 2A8
  nuclear properties, 2A7
Californium-252
  fission products, decay schemes, 5A7
  fission, prompt neutron studies, 5A17
  production of gram quantities for neutron irradiation facility, 2A33
  spontaneous fission properties, 2A20
Californium chlorides ($CfCl_3$)
  crystal structure studies, 5A42
Californium fluorides
  preparation, 2A60
Californium oxychloride
  crystal structure studies, 5A42
Calorimetry
  bomb type, determination of enthalpy of formation of diborides, 2B10
  bomb type, determination of enthalpy of formation of silicon carbide, 2B11
  bomb type, determination of enthalpy of formation of tetrafluoromethane, 2B11
  bomb type, determination of enthalpy of formation of uranium compounds, 2B12
  development of high-temperature, high-pressure, adiabatic, 8C3
  drop type, development of instrument for high precision enthalpy measurements, 2B13
  flow type, determination of enthalpy of formation of uranium compounds, 2B12
  heat effects of current across interfaces, 6-9
  ion exchange studies, 8A14
  low temperature heat capacity measurements, 2A80
  at low temperatures, 5B24
  of molten salts, 8C9
  study of complexes in fused salts, 6-10
  uranium-235m decay energy determination, 5A12
Camphor
  optical rotatory dispersion studies, 2A57
Capacitance measurements
  surface adsorption studies by, 1A16
Carbamates
  isotope exchange reaction with carbon dioxide, 8A27
Carbides
  high temperature chemical and physical studies, 2A54
  neutron diffraction studies, 2A74
Carbon
  absorption coefficient measurement, 5B5
  combustion in fluorine, enthalpy determination, 2B11
  determination by helium-3 activation analysis, 5A57
  determination in submilligram samples of organic compounds, 5A71
  hot-atom chemistry, 3A6
Carbon-10
  (p,t) reaction, nuclear energy level studies, 5A27
Carbon-11
  recoil chemistry, 1A29
  recoil fragments, range-energy studies, 2A10
  recoil fragments, range-energy studies, 2A11
Carbon-12
  $(\alpha,\alpha'\gamma)$ reaction, angular correlation studies, 5A33
  (p,t) reaction, nuclear energy level studies, 5A27
Carbon-12 ions
  bombardment of thulium to produce rhenium-181, 5A21
  irradiation of rare earths for platinum isotope production, 5A11
Carbon-13
  analysis by mass spectrometry, 3A13
Carbon-14
  tetraalkyl ammonium ion labeling for ion exchange studies, 8A14
Carbon-16
  formation cross sections, 3A1
Carbon dioxide
  effects on synthesis of water from hydrogen and oxygen, 8A34
  isotope exchange reaction with carbamate, 8A27
Carbon dioxide systems (CO_2-HD)
  energy transfer in ion-molecule interactions of, 3A10
Carbon ions
  bombardment of californium for production of heavier elements, 5A5
Carbon monoxide
  diffusion studies, 8C11
Carbon monoxide systems (CO-HD)
  energy transfer in ion-molecule interactions of, 3A10
Carbon nitride
  absorption coefficient measurement, 5B5
  determination of radiative lifetime in excited state, 5B3
Carbon tetrafluoride
  enthalpy of formation, 2B11
  formation by radiolysis of inorganic fluorides in presence of carbon, 8C2
  molecular complexity of organo-phosphorus compounds in, 2A86
Carbonates
  spectral studies, 2A87
Carbonium ions
  prototype reactions of, 3A9
  studies as intermediate in deamination reactions, 8A30
Carbonyl nitro phenol
    (See Phenols, carbonyl nitro-)
Carbonyl phenol
    (See Phenols, carbonyl-)
Carboxylic acid polymers, polyamino-
    (See Acids)
Catalysis
  effect of strong acids, 5A61
  by platinum, effect of stored energy, 7-21
  radiation chemical studies, 8A34
Cathodes
  refractory metals, corrosion in hydrogen fluoride solution, 8A18
Cations
  behavior in aqueous solutions at high temperature, 8C5
  comparison of activity coefficients with anions, 2A82
  interactions in aqueous solutions, theoretical studies, 2A81
  interaction with anions, spectral studies, 2A65
Centrifugation
    (See Ultracentrifugation)
Ceramics
  sintering of thoria gel, 8D14
Cerium
  hydrolysis studies, 3B8
Cerium (liquid)
  extraction from liquid chromium-uranium eutectic by liquid magnesium, kinetics studies, 5B19
Cerium-130
  half life, 5A6
Cerium-135
  decay scheme, spectrographic observations, 8A8
  energy-level diagrams, 8A8
  isomeric transition, 8A8
Cerium-143
  nuclear spin determination, 5A13
Cerium alloys (Cd-Ce)(liquid)
  phase studies, 2B4

  thermodynamic properties, 2B3
Cerium alloys (Ce-Zn)(Liquid)
  phase studies, 2B4
Cerium halides
  electronic conductivity of metal solutions, 1A20
Cesium
  bombardment with oxygen-16 ions, fission excitation function measurements, 5A21
  photosensitized ionization, 5B15
Cesium-129
  production of pure, 3B10
Cesium-132
  production of pure, 3B10
Cesium cadmium chlorides ($CsCdCl_3$)
  crystal structure, x-ray diffraction studies, 2A71
Cesium - cesium bonds
  energy, 5B15
Charge transfer
  radiation chemical studies in gases, 8A34
  regenerative cell kinetics studies, 2B9
Charged particles
  elastic and inelastic scattering studies, 5A34
  interaction mechanism with complex nuclei, 5A24
  range-energy relationship in matter, 5A23
  tracks, reaction studies in radiation chemistry, 7-19
Chelates
    (See also Complexes)
  formation in solvent extraction, 4-2
  hydrogen bond strength studies, 2A82
  interaction with rare earths, absorption spectra studies, 2A61
  interaction with rare earths, absorption spectra studies, 2A62
  metal complexing by, water exchange rate studies, 5B6
  physico-chemical characterization by mass spectrometry, 1A17
  polyamino polycarboxylic acid use in transplutonium element separations, 2A90
  potentiometric studies, 7-33
  properties of polyfunctional ligands with di-, tri-, and tetra- valent metal ions, 7-35
  rare earth ion spectral studies, 2A76
  of transitional metals, infrared spectra, 7-39
Chemical bonds
    (See Bonds)
Chemical equipment
    (See Equipment and specific devices, e.g., Liquid-liquid settlers)
Chemical reactions
    (See Reactions)
Chlorates
  radiolysis, LET effects, 8A34
Chloride ions
  effect on oxidation of chromium ion by thallium ions, 3A8
  effect on thallous-thallic exchange, 3A8
  reactions with iron ions, 3A8
Chlorine
  reaction rate with uranium tetrachloride, 5B18
  surface reactions with molybdenum and yttrium, 6-1
Chlorine-35
  enrichment by ion exchange, 1A26
Chlorine-37
  enrichment by ion exchange, 1A26
Chlorine fluorides (ClF_3)
  Raman spectroscopy of solutions using laser light source, 2A67
p-Chloroaniline
  complexes with metal halides, dissociation in solution, 7-30
Chlorophyll
  deuteriated, reactivity studies, 2A51
  role in photosynthesis, study by chromatography, 2A32
Chlorosalicylaldehyde
    (See Salicylaldehydes, chloro-)
Chromate ions
  corrosion inhibition by, 8A16
Chromatography
  development, 2A32
  reversed-phase, analytical separations by, 1A4
  use of bifunctional organophosphorus compounds, 1A2
Chromatography (vapor phase)
  organogermanium alkoxides, 7-36
Chromium
  chronopotentiometry in molten fluorides, 8B2
  solvent extraction from acid solutions by amines, 8D3
  valence state produced by radiolysis of aqueous solutions, 8A33
Chromium-51
  tracer studies on corrosion inhibitors, 8A16
Chromium-52
  alpha particle reactions, 2A4
Chromium alloys (Cr-U)(liquid)
  liquid metal extraction studies using, 5B19
Chromium carbides (Cr_3C_2)
  neutron diffraction studies, 2A74
Chromium chloride ions
  decomposition kinetics, 1A15
Chromium intermetallic compounds ($AlCr_2$)
  neutron diffraction studies, 2A74
Chromium iodide ions
  decomposition kinetics, 1A15
Chromium ions
  catalysis of chromium chloride ion decomposition, 1A15
  complexes with DL-phenylalanine, infrared spectra, 7-39
  complexes with hydrophosphorous ions, 1A15
  complexes with hypophosphite ions, 1A15
  oxidation by thallium ions, effects of chloride ions, 3A8
Chromium oxide systems (Cr_2O_3-ZnO)
  diffusion studies, 7-24
Chromium oxides (Cr_2O_3)
  neutron diffraction studies, 3A12
Chromium uranates
  crystal structure, x-ray diffraction studies, 2A71
  uranium-oxygen bond studies, 2A78
Chronopotentiometers
  development for molten-salt applications, 8B3
  of metal solutions in molten halides, 3B1
Chymotrypsin
  denaturation at low temperatures by aqueous solvents containing methanol, 3A11
  reactions, low temperature studies, 3A11
Cinnamic acid, phenyl-
  radiation chemical studies of isomers of, 2A40
Citric acid monohydrate
  neutron diffraction studies of structure, 8A35
Coalescence
  effect of ionizing radiation, 8D5
Cobalt-58g
  production by $Fe^{58}(t,n)Co^{58}$ reaction, 3B10
Cobalt halides
  complexes with aryl amines, dissociation in solution, 7-30
Cobalt ions
  complexes with dibasic amino acids, infrared spectra, 7-39
  complexes with hexamine, chemical effects of gamma rays, 1A22
  complexes with DL-leucine, infrared spectra, 7-39

  - complexes with DL-norvaline, infrared spectra, 7-39
  - complexes with DL-phenylalanine, infrared spectra, 7-39
  - oxidation of iron ions in presence of chloride ions, 3A8
- Cobalt, tris (ethylenediamine)-
  - gamma radiation, chemical effects, 1A22
- Cobalt uranates
  - crystal structure, x-ray diffraction studies, 2A71
  - uranium-oxygen bond studies, 2A78
- Coincidence spectroscopy
  - development for activation analysis, 2A34
  - energy level determination for fermium-255 decay products, 5A10
  - energy-level studies, 8A5
  - heavy nuclei, energy level studies, 8A2
  - pulse-height analyzer design, 8A6
  - radioactive decay studies, 2A23
- Color centers
  - in crystals, spectroscopic studies, 7-22
- Complexes
  - (See also Chelates, Coordination chemistry, and complexes by name, e.g., Hexaminecobalt complexes)
  - actinides, bonding, 4-1
  - actinides, chemical bonding studies, 4-3
  - chemistry of vic-dioximes, 1A3
  - formation in solvent extraction, 4-2
  - in fused salts, calorimetric studies, 6-10
  - infrared spectra, 7-31
  - inorganic ions in aqueous solution, 8A12
  - metal halides with aryl amines, dissociation in solution, 7-30
  - structural chemistry, 1A11
- Compound nuclei
  - decay scheme as function of formation mechanism, 5A29
- Computers
  - application to diffraction experiments, 1A10
  - assymetric rotor nuclear model studies, 2A77
  - beta spectra analysis by, 2A24
  - calculation of ionization intensity functions for rare gases, 2A85
  - calculations for rare earth spectral analysis, 2A76
  - crystallography studies, 3A12
  - Hamiltonian equation studies of rate processes, 3A7
  - isotope effects studies, 3A7
  - nuclear reaction theoretical calculations, 2A70
  - nuclear shell model calculations, 5A14
  - nuclear structure calculations, 5A15
  - for study of ions in the gas phase, 7-18
  - theoretical nuclear chemistry calculations, 2A69
  - thermodynamic studies on aqueous solutions, application to, 8A13
  - tri-variate inverse interpolation, 2A77
  - for x-ray diffraction patterns, 4-3
- Conductivity
  - (See Electric conductivity)
- Conductometric titrators
  - development of highly sensitive, 8B3
- Configuration interactions
  - spectra, 5A43
- Contactors
  - gas-liquid, mathematical analysis, 8D7
- Conversion electrons
  - (See Electrons and Internal conversion)
- Coordination chemistry
  - (See also Complexes)
  - actinide elements, 4-1
  - metal ions in fused salts, 2A63
  - rare earths, 2A65
- Copper
  - complexes with vic-dioximes, 1A3
  - isotope exchange reactions, 8A27
  - nuclear magnetic field studies, 5A47
- Copper-65
  - (p, pπ^+) reaction, 2A13
- Copper complexes
  - structure and magnetic properties, 1A11
- Copper halides
  - complexes with aryl amines, dissociation in solution, 7-30
- Copper ions
  - complexes with dibasic amino acids, infrared spectra, 7-39
  - complexes with DL-leucine, infrared spectra, 7-39
  - complexes with DL-norvaline, infrared spectra, 7-39
  - complexes with DL-phenylalanine, infrared spectra, 7-39
  - complexes with glycine, infrared spectra, 7-39
- Copper(II) ions
  - alkylhydroxy substituted pyridine complexes, formation constants, 7-33
  - half-wave potential and diffusion current in solutions, 7-33
  - reduction kinetics, 8C4
- Copper uranates
  - crystal structure, x-ray diffraction studies, 2A71
  - uranium-oxygen bond studies, 2A78
- Correlation coefficients
  - in proton-proton scattering reactions, 5A30
- Corrosion
  - in fused-salt systems, electrochemical studies, 8D16
  - organic ion adsorption effects, 8A17
  - refractory metals, kinetic studies, 8A18
- Corrosion inhibitors
  - electrochemical reactions, effect on, 8A16
- Cosmic radiation
  - nuclear chemistry studies, 3A3
- Coulomb excitation
  - studies with heavy ions, 5A36
- Coulomb scattering
  - alkali atom beams with halogens, 8A20
- Coulometry
  - generation of Cr^{++} in sulfuric acid solutions, 7-37
  - instrument development, 8B3
  - titration of alkaline earth cations, 1A1
- Counting (radiation)
  - gamma rays in magnetic fields, 5A2
- Covalence
  - inorganic salts, spectral studies, 2A87
- Crab
  - (See Horseshoe crab)
- Cross sections
  - alkali atom collisions with halogens, 8A20
  - fission, heavy-ion induced reactions, 5A21
  - fluctuations for nuclear reactions, 2A6
  - for formation of metastable molecular states, 5A44
  - isomeric ratio studies, 2A3
  - measurement for the $Ni^{58}(t,n)$ Cu^{60} reaction, 3B10
  - neutron, of actinide elements, 2A8
  - neutron capture, mass spectrometry measurements, 8A22
  - neutron reactions, measurement, 8A7
- Crustaceans
  - (See Horseshoe crab)
- Crystal structure
  - (See also Neutron diffraction analysis)
  - actinide compounds, 4-3
  - of actinides and lanthanides, 5A42
  - diffraction experiments, computer applications, 1A10
  - effects on radiolysis of bromates and nitrates, 8A34
  - magnetic materials, 3A12
  - magnetic materials, neutron diffraction studies, 3A12
  - neutron diffraction studies, 8A35
  - uranates, 2A78

  - uranates, x-ray diffraction studies, 2A71
  - uranium oxides, 2A78
  - uranyl salts, 2A78
  - x-ray diffraction studies, 5A41
- Crystals
  - diffusion in ionic, 7-24
  - ionic, spectroscopic study of color centers, 7-22
  - irradiation, paramagnetic resonance spectroscopy, 8A10
  - neutron diffraction studies, 8A35
  - radiation chemical studies, 8A32
  - single, production techniques, 2A74
  - x-ray diffraction studies, 4-3
- Cupric ions
  - (See Copper(II) ions)
- Curium
  - atomic spectra studies, 5A56
  - crystal-structure studies, 5A54
  - emission spectroscopy, 2A72
  - ions, solid-state spectra studies, 5A55
  - spectrophotometry of solutions at high temperatures and pressures, 8D15
- Curium-238
  - production, 2A1
- Curium-240
  - nuclear properties, 2A7
- Curium-241
  - decay studies, 2A23
  - nuclear properties, 2A7
- Curium-242
  - use in neutron source for irradiation facility, 2A33
- Curium-244
  - neutron cross sections, 2A8
- Curium-245
  - fission, mass distribution studies, 2A14
- Curium-246
  - neutron cross sections, 2A8
  - nuclear properties, 2A7
- Curium-247
  - neutron cross sections, 2A8
  - nuclear properties, 2A7
- Curium-248
  - fission properties, 2A20
  - neutron cross sections, 2A8
  - nuclear properties, 2A7
- Curium chlorides ($CmCl_3$)
  - thermal expansion and crystal structure, 5A42
- Curium fluorides
  - preparation, 2A60
- Curium ions
  - electronic energy level studies, 5A52
  - thermodynamic data, 5A53
- Curium oxides
  - preparation in fused salt solutions, 2A62
- Curium oxides (CmO_2)
  - vapor pressure, 2A60
- Cyclohexane
  - deuterated, effect on pi-complex formation, 3A7
  - solutions, energy transfer in luminescence, 7-8
  - vacuum ultraviolet photochemistry, 7-2
- Cyclohexane, perfluoro-
  - radiation and heat, effects on, 3B3
- Cyclo-hexyl group
  - effects on extraction effectiveness of organophosphorus compounds, 2A88
- Cyclopropane, 2-diphenyl-
  - radiation chemical studies of isomers of, 2A40
- Cyclotrons
  - alpha particles for (α,d) reactions with light nuclei, 5A28
  - high energy charged particles for nuclear reaction studies, 5A24
  - protons for induction of two-nucleon pickup reactions, 5A27
- Cytosine
  - absorption spectra of hydrated electrons in aqueous solutions of, 2A43
- Data processing
  - instrument design for coincidence spectroscopy, 8A6
- Deamination reactions
  - studies of intermediates, 8A30
- Decalin, perfluoro-
  - radiation and heat, effects on, 3B3
- Decay
  - (See Radioactive decay)
- Decomposition
  - (See also Photolysis, Pyrolysis, and Radiolysis)
  - dialkyl azo compounds, deuterium isotopic effects, 3A7
  - uranyl metaborate, 2A78
- Decyl alcohol
  - molecular complexity of organo-phosphorus compounds in, 2A86
  - molecular complexity of organophosphorus compounds in, 2A89
- Dehydration
  - alcohols, as carbonium ion prototype reaction, 3A9
- Dehydrogenation
  - (See Allomerization)
- *Desulfovibrio*
  - reduction of sulfate ion to hydrogen sulfide, 5A69
- Deuterides
  - low temperature calorimetric studies, 2A80
- Deuterium
  - chelate labeling, bond strength studies, 7-39
  - π complexes, 8A28
  - determination in water by spectroscopy, 3A13
  - effects on infrared spectroscopy and molecular constants, 6-8
  - effects on photosynthesis, 2A51
  - effects on properties of proteins, 2A52
  - kinetic effects in hydrogen abstraction reactions of trifluoromethyl radical, 3A7
  - labeling of compounds in plants grown in heavy water, 2A50
  - modulated molecular beams, interaction with heated surfaces, 8A21
- Deuterium chloride
  - heavy-water solution, activity coefficient studies, 8A13
- Deuterium oxide
  - (See Water (D_2O))
- Deuterium systems (CO-HD)
  - energy transfer in ion-molecule interactions of, 3A10
- Deuterium systems (CO_2-HD)
  - energy transfer in ion-molecule interactions of, 3A10
- Deuterium systems (HD-N_2)
  - energy transfer in ion-molecule, interactions of, 3A10
- Deuterium systems (HD-N_2O)
  - energy transfer in ion-molecule interactions of, 3A10
- Deuterium systems (HD-O_2)
  - energy transfer in ion-molecule interactions of, 3A10
- Deuterons
  - bombardment of targets in studies of nuclear reactions, 5A24
  - proton scattering and polarization at high energy, 5A26
- Dialkylphosphinyl alkanes
  - use as solvent extractants, 1A2
- Diaminobenzene
  - reduction studies, 3B8
- Diatoms
  - chlorophyll reactivity studies, 2A51
- Diaphrams

(See Membranes)
Diasteroisomers
  identification by nuclear magnetic resonance spectroscopy, 8A29
Diazonium fluoborates
  thermal decomposition, isotope effects, 8A27
Dibenzoyl methane
  structure, 1A11
Diborane
  deuterated, infrared spectroscopy, 6-8
Dicarboxylic acids
  chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
Dichloro (ethylenediamine) platinate(II)
  substitution reaction rates, 1A24
Dicupferron
  chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
Di 2-ethyl hexyl phosphoric acid
  (See Phosphoric acid, di 2-ethyl hexyl-)
Differential migration
  chemical analysis by, 2A32
Diffraction experiments
  (See also Neutron diffraction analysis)
  computer applications, 1A10
  liquid structure studies, 8A24
Diffusion
  effect on oxygen reaction with refractory metals, 5B20
  in molten salts, measurements, 8C3
Diffusion chambers
  design and fabrication, 8C11
Diffusion coefficients
  measurement as function of temperature, 7-26
Diluents
  effect on extraction of rare earths by organophosphorus compounds, 2A89
  molecular complexity of organo-phosphorus compounds in, 2A86
Dimethyl sulfoxide
  electromotive series in, 5B30
Dimethylglyoxime
  irradiated single crystals, paramagnetic resonance spectroscopy, 8A10
Dinaphthazarin
  chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
Dinonylnaphthalene sulfonic acid
  (See Sulfonic acids, dinonylnaphthalene-)
Dioaxane
  water solutions, polarography of ions and complex compounds in, 7-33
Diodes
  fission fragment velocity measurements, 5A17
Dioximes
  chemical studies, 1A3
Di para (1,1,3,3-tetramethyl butyl phenyl) phosphoric acid
  (See Phosphoric acid, di para (1,1,3,3-tetramethyl butyl phenyl))
Diphenyl
  solutions in aliphatic alcohols, solvated electron studies, 2A41
Diphenyl, tetrachloro-
  separation from water, design of liquid-liquid settler, 5A68
Diphenyl-2-butene germanium complex
  structure, 1A11
Diphenylbutanediol
  isomers, identification by nuclear magnetic resonance spectroscopy, 8A29
2-Diphenylcyclopropane
  (See Cyclopropane, 2-diphenyl-)
Diphosphopyridine nucleotide
  reactions at low temperatures, 3A11
Diquinone, naphtha-
  chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
Disproportionation
  organogermanium alkoxides, 7-36
Dose (radiation)
  effects on radiolysis, 8A33
Droplets
  mass transfer from, in solvent extraction columns, 1B1
Dysprosium
  absorption spectra in oxy-acetylene flames containing ethanol solutions of perchlorates, 1A8
  atomic spectra studies, 5A56
Dysprosium-161
  mossbauer effect under high pressure, 5B13
Dysprosium oxides (Dy_2O_3)
  phase studies at high temperatures and pressures, 2A56
Earth
  nuclear geochemistry, 5A5
Economics
  thorium reserves and process costs, 8D10
  uranium and thorium processing, improvements, 8D12
Effusion
  phase studies of lanthanide rare earth-group IIB intermetallics, 2B4
Einsteinium
  alpha particle emission, angular distribution studies, 5A1
  compounds, crystallography, 5A42
  oxidation in aqueous solutions, 2A60
  spectrophotometry of solutions at high temperatures and pressures, 8D15
Einsteinium-253
  decay, electron spectrometry studies, 5A4
Einsteinium-254m
  decay scheme, 5A10
Einsteinium fluorides
  preparation, 2A60
Electric charge
  transport in electrochemical systems, 5B29
Electric conductivity
  (See also Superconductivity)
  of aqueous solutions at high temperature and high pressure, 8C6
  xenon fluorides in hydrogen fluoride and halogen fluoride solutions, 2A67
  of water, transient effects of pulse irradiation, 2A46
Electric discharges
  free radical reactions, studies on CH_2 and NH, 7-1
Electric resistance
  metals at high pressure, 5B11
  metals, use in determination of temperature at high pressures, 5B10
Electric resonance spectroscopy
  of molecular beams, 5A46
Electrochemistry
  bimetallic regenerative cell studies, 2B7
  calcium in liquid ammonia, 5B30
  corrosion inhibition by organic ion exchange, 3A17
  coulometric generation of Cr in sulfuric acid solutions, 7-37
  current distribution studies in porous electrodes, 5B28
  dimethyl sulfoxide systems, 5B30
  electrode - electrolyte reactions, 5B27
  of fused salts, 3B9
  of fused salts, 8D16
  of high-temperature systems, 5B1

kinetics, effect of corrosion inhibitors, 8A16
liquid phosphorus in aqueous media, 5B30
lithium hydride systems in regenerative cells, 2B6
of molten salts, 8B2
passive oxide layers on refractory metals, studies on, 8A18
polarographic studies of metal ions in sulfuric acid solutions, 7-37
properties of electrolyte interfaces, 6-9
regenerative cell kinetic studies, 2B9
thermodynamic properties determination for binary liquid metal solutions, 2B3
transport phenomena studies, 5B29

Electrochromatography
development, 2A32

Electrodes
(See also Cathodes)
development for E.M.F. studies in molten fluorides, 8C9
kinetics studies in regenerative cells, 2B9
porous, current distribution studies, 5B28
reactions with electrolytes, 5B27
second order, nonaqueous system studies, 5B30
use in analytical chemistry, radiation effects, 8B4

Electrolysis
pulse techniques, regenerative cell studies, 2B9

Electrolytes
aqueous solutions, thermodynamic studies, 8A13
dynamic processes, nuclear magnetic resonance studies, 2A84
heat effects of current across interfaces, 6-9
hydrogen activity of potassium chloride, 2A82
ion-ion interactions, theoretical studies, 2A81
ion-solvent interactions, theoretical studies, 2A81
polyelectrolytes, ion exchange, 8A14
reactions with electrodes, 5B27
structure, nuclear magnetic resonance studies, 2A84
thermodynamic data compilation, 6-11
transport properties, 5B29

Electromagnetic fields
separation of recoil atoms from beam of bombarding ions using, 5A5

Electromotive series
in dimethyl sulfoxide, 5B30

Electron diffraction analysis
hexafluorides, thermodynamic studies, 2A80
studies on gas molecules, 1A9

Electron micrography
of thoria gels, 8D14

Electron paramagnetic resonance
of actinide ions, study of electronic energy levels, 5A52
crystal symmetry effects, 2A73
free radical studies at cryogenic temperatures, 7-25
of peroxo-dicobalt complexes, 2A73
photosynthesis studies using deuteriated algae, 2A51
of quartz, radiation damage and charge-transfer studies, 2A73
radiation chemistry studies by, 7-12
reaction rate studies of gaseous free radicals, 5B17
spectroscopy of irradiated single crystals, 8A10
sulfur - nitrogen ions in solution, 5B7

Electron transfer
scattering of alkali atoms by halogens, 8A20

Electronic equipment
pulse amplifiers, design and development, 5A39

Electronic states
radiation excitation, fundamental studies, 7-17

Electrons
(See also Beta particles)
bonding studies in fluorine, 5B25
configuration in alloys and compounds, Mossbauer effect studies, 5A48
conversion, angular anisotropy of emission from oriented nuclei, 5A1
conversion, nuclear structure studies using, 5A3
conversion, relation to fragment mass in prompt fission, 5A17
effects on aqueous solutions, 2A42
effects on fluorocarbons, 3B3
exchange processes in oxidation-reduction reactions, 3A8
gaseous reaction kinetics, 5B16
hydrated, absorption spectra in aqueous solutions, 2A43
hydrated, pulse radiolysis studies of free radical reactions, 2A42
hydrated, studies in hydrogen-saturated, alkaline aqueous solution, 2A44
hydrated, studies in pulse irradiated water, 2A46
hydrated, transient absorption spectrum studies, 2A42
impact with molecules and atoms, 7-15
rare gas ionization by, experimental threshold laws, 2A85
solvation in radiation chemistry of aliphatic alcohols, 2A41

Electrophoresis
deuteriated proteins, 2A52

Electrostatic fields
separation of recoil atoms from beam of bombarding ions using, 5A5

Element number 104
search for by bombardment of californium with heavy ions, 5A5

Element number 105
search for by bombardment of californium with heavy ions, 5A5

Elements (heavy)
(See also specific elements by name)
fission-spallation reactions with high-energy protons, 2A9
fission, yield studies by nuclear chemistry, 8A3
nuclear energy level studies, 8A2
nuclear properties, 2A7

Elements (light)
(See also specific elements by name)
analysis by Rutherford scattering, 2A28
isotope separation by ion exchange, 1A26
isotope separation by isotopic exchange, 8A27

Ellipsometry
electrode - electrolyte interface studies, 5B27

EMF measurements
on metal halide - metal solutions, 1A20
of molten salts, 8C9
of molten salts and liquid metals, 3B1

Emission spectrography
(See Spectra (emission))

Energy
kinetic, of fragments from heavy ion-induced fission, 5A20
stored, effect on catalytic activity of platinum, 7-21

Energy levels
of actinide ions, study by paramagnetic resonance, 5A52
of free-atom actinides, 5A56

Energy transfer
gas phase reactions, 3A10
in molecular systems, 7-20
radiolysis of alkali halide systems, 8A34

Enthalpy
changes of electrochemical reactions, measurement, 6-9
determination using high percision drop type calorimeter, 2B13
diboride formation with Group IV and V metals, 2B10

  low temperature calorimetric studies, 2A80
  silicon carbide formation, 2B11
  sodium vaporization, 2B2
  tetrafluoromethane formation, 2B11
  transition element compounds, measurement, 8A11
Entropy
  calorimetric determinations of half-cell, 6-9
  low temperature calorimetric studies, 2A80
  transition elements and compounds, measurement, 8A11
Enzymes
    (See also specific enzymes, e.g., Chymotrypsin, Lactic acid dehydrogenase, etc.)
  deuteriated, properties of, 2A52
  reactions, low temperature studies, 3A11
  role in learning process of planarians, 3A11
Equipment
  turbulent transport of heat, mass, and momentum, 1B7
Erbium
  reaction with its molten chloride and iodide, 1A20
Erbium-165
  hyperfine sturcture studies, 5A13
Erbium intermetallic compounds ($ErMn_2$)
  neutron diffraction studies, 3A12
Erbium oxides (Er_2O_3)
  phase studies at high temperatures and pressures, 2A56
Erythro- isomers
  identification by nuclear magnetic resonance spectroscopy, 8A29
Ethane
  modulated molecular beams, interaction with heated platinum surfaces, 8A21
  photochemistry, 6-3
  radiolysis, effects of density, 7-6
Ethanol
  solvated electron absorption spectra, 2A41
Ethene
  ions, structure, 7-15
Ethers
    (See also specific ethers by name e.g., Butyl ether, Methyl ether, etc.)
  di-alkyl, molecular complexity of organo-phosphorus compounds in, 2A86
  solvent extraction studies, 4-2
Ethyl ether
  boron trifluoride complexes, Raman and infrared spectra, 8A26
2-Ethyl hexanoic acid
  molecular complexity of organo-phosphorus compounds in, 2A86
Ethyl radicals
  ions, structure, 7-15
Ethylenediamine
  ion exchange with alkali metals, isotope separation by, 8A27
Ethylmagnesium bromide
  structure, 1A11
Europium
  absorption spectra in oxy-acetylene flames containing ethanol solutions of perchlorates, 1A8
  electronic configuration, Mossbauer effect studies, 5A48
  isolation by ion exchange, 1A25
  valence state produced by radiolysis of aqueous solutions, 8A33
Europium ions
  heats of formation, 5A53
Europium oxide
  heat of formation, 5A53
Evaporation
    (See Volatilization)
Excitation functions
  for metastable electronic states in molecules, 5A44
Extractants
  effectiveness of organophosphorus compounds, effects of various substituted groups, 2A88
  organophosphorus compounds, molecular complexity in diluent solutions, 2A86
Fermi-Dirac systems
  liquid helium-3 studies, 2A79
Fermium
  spectrophotometry of solutions at high temperatures and pressures, 8D15
Fermium-254
  fission properties, 2A20
Fermium-255
  decay scheme, 5A10
Fermium-256
  fission properties, 2A20
Ferrites
  diffusion phenomena during sintering, 7-24
Ferrocyanide ion
  radiation chemical studies of solutions of, 2A44
  reduction by borohydride ion, 5B8
Ferromagnetic materials
  heat capacities at low temperatures, 5B24
Ferromagnetism
  induced internal fields, 5A47
  in solids, fundamental studies, 1A12
Filaments
  for surface ionization in high temperature chemistry studies, 2A53
Fission
  of actinide elements, 2A20
  by alpha particles, 2A5
  fundamental studies, 2A14
  fundamental studies, 2A18
  half-lives for spontaneous, 5A18
  heavy-ion-induced, fission cross section studies, 5A21
  heavy-ion-induced, kinetic energy measurement of fission fragments, 5A20
  by helium ions, kinetic energy studies, 2A19
  intermediate energy studies using mass spectrometry, 5A22
  isomer yields, 2A14
  near-threshold, of uranium-235
  prompt radiations in, 5A17
  radiochemical studies in targets bombarded with charged particles, 5A24
  spontaneous, mass and energy distribution of fragments, 5A19
  studies with high-energy protons, 2A9
  tritium production, scintillator studies, 2A26
  yields, automatic data recording, 8A6
  yields, nuclear chemistry studies, 8A3
Fission barriers
  determination from heavy-ion bombardment of various elements, 5A21
  measurement and interpretation, 5A16
Fission products
  angular studies, 3A1
  chemical reactions induced by, 5B23
  delayed neutron emission, 8A5
  detection of, fission barrier studies, 5A16
  detection by mica sheets, 5A40
  gamma rays and neutrons from, 2A17
  initiation of chemical reactions, 3B6
  kinetic energy measurements in heavy-ion-induced fission, 5A20
  kinetic energy studies, 2A19
  kinetic energy studies, 2A20
  mass determination by observation of prompt gamma rays,

5A17
- mass distribution studies, 2A18
- mass and energy distribution studies, 5A19
- mass spectrometric analysis, 3A13
- nuclear energy level studies, 8A5
- scintillator interactions, 2A26
- solvent extraction from acid solutions by amines, 8D3
- spin studies, 2A14
- yield measurement by direct mass spectrometry, 5A22

Flames
- spectroscopy, 1A7

Flash photochemistry
- study of excited molecules, 6-3

Flash spectroscopy
- of free radicals at cryogenic temperatures, 6-5

Flow calorimetry
- (See Calorimetry)

Fluid flow
- heat and mass transfer, 5A74
- mass transfer in gas-liquid systems, 5A76
- turbulent exchange of momentum and mass at a wall, 5A70
- turbulent transport of heat, mass, and momentum, 1B7

Fluidized particles
- use to study liquid kinetics, 5A63

Fluometry
- determination of various metal ions using, 7-38

Fluorescence
- (See also Luminescence)
- benzene, quantum yield for, 2A49
- polarization studies, 5B4

Fluorescent compounds
- determination of radiative lifetime in excited state, 5B3

Fluoride ions
- interaction with rare gas cations, theoretical studies, 2A81
- solvation, solvent extraction studies, 5A50

Fluoride volatility processes
- basic chemistry studies, 8D16
- solvent studies, 3B4

Fluorides
- gaseous, thermodynamic properties, 6-6
- irradiation of inorganic, fluorine release, 8C2
- molten, electrochemistry, 8B2
- molten, physical chemistry studies, 8C9
- phase studies, 8C10

Fluorine
- combustion of carbon ion, enthalpy determination, 2B11
- determination by helium-3 activation analysis, 5A57
- molecular structure studies by nuclear magnetic resonance, 5B25
- release from irradiated inorganic fluorides, 8C2
- surface reactions with nickel, 6-1

Fluorine-18
- excitation of spin-5 level in $O^{16}(\alpha,d)F^{18}$ reaction, 5A28
- production by trition interaction, 3B10

Fluorocarbons
- radiation and heat, effects on, 3B3

Fossils
- dating by isotopes, 3A3

Fragmentation
- radiochemical studies in targets bombarded with charged particles, 5A24

Free energy
- intermetallic compound formation in binary liquid metal solutions, 2B3
- lithium hydride formation, 2B6
- low temperature calorimetric studies, 2A80

Free energy functions
- transition elements and compounds, measurement, 8A11

Free radicals
- aromatic substitution, 7-27
- flash spectroscopy at cryogenic temperatures, 6-5
- formation by irradiation of pure substances, 8A10
- hydrazyl-type, magnetic resonance studies of chemistry of, 2A73
- production in organic oxidation reactions, 1A14
- reactions of CH_2 and NH in electrical discharges, 7-1
- reaction rate studies by electron paramagnetic resonance, 5B17
- study at cryogenic temperatures, 7-25
- yields in radiolysis of organic systems, 7X2

Fuel element reprocessing
- dissolution studies, 3B4
- fused salt - molten metal extraction, 1B2

3,4-Furandicarboxylic acid
- deuterium isotope effect in, 1A11

Fused salts
- actinide complexes in, 4-3
- chemical properties at high temperature, 7X1
- chlorination rate of uranium tetrachloride in, 5B18
- complexes in, calorimetric studies, 6-10
- coordination number studies of various metal ions, 2A63
- electrochemical studies, 3B9
- electrochemical studies, 8D16
- electrochemistry, 8B2
- fluorides, phase studies in, 8C10
- halides, interaction with metals, 1A20
- halides, physical and chemical properties, 1A19
- liquid structure, diffraction studies, 8A24
- metal freezing by, in liquid metal extraction studies, 5B19
- metal solutions in, 8A25
- metal solutions, spectrophotometry and chronopotentiometry, 3B1
- molecular interactions in, 4-1
- molten metal extraction studies, 1B2
- phase studies in regenerative cells, 2B6
- phase studies in regenerative cells, 2B7
- physical chemistry studies, 8C9
- rare earth nitrate crystal growth in, 2A61
- rare earth studies in, 2A62
- solubility of intermetallic compounds in, 2B8
- thermodynamic properties, 5A62

Fused salt volatility processes
- (See Fluoride volatility processes)

G-values
- for hydrated electron formation in tetranitromethane solutions, 2A44
- for solvated electron formation in ethanol, 2A41

Gadolinium
- absorption spectra in oxy-acetylene flames containing ethanol solutions of perchlorates, 1A8

Gadolinium-153
- nuclear spin determination, 5A13

Gadolinium chlorides
- magnetic susceptibility measurements, 1A19

Gallium-62
- production, 2A1

Gallium alloys (Ga-U)(liquid)
- thermodynamic properties, 2B3

Gallium intermetallic compounds ($HoGa_2$)
- neutron diffraction studies, 3A12

Gamma radiation
- automatic counting instrument, 8A6
- counting in magnetic fields, 5A2
- divalent rare earth preparation using, 2A61
- effect on cis-trans isomerization of stilbene in benzene, 7-4
- effects on deuteriated proteins, 2A52

   effects on xylene isomers, 2A48
   energy measurements, Mossbauer effect, 5A48
   from fission fragments, 2A17
   fluorescence excitation of rare earths, 2A61
   hydrocarbon luminescence by, 7-11
   nuclear, angular correlation, 5A47
   prompt emission in fission, 5A17
   radiation chemical studies using organic compounds, 2A40
   radiolysis of alkali metal and alkaline earth halates, 8A32
Gas-liquid contacting equipment
   mass transfer in, 5A67
Gaseous diffusion
   fundamental studies, 8C11
Gases
   chemical reactions, identification of intermediate species, 5B26
   interaction with solid surfaces, 1A16
   interaction with solids, molecular beam studies, 2A55
   ionized, rates of charge neutralization, 5B14
   mass transport in plant equipment, 1B7
   molecular excitation and reactions, 3A10
   molecular structure and internal motion studies, 1A9
   photoionization studies, 6-4
   radiation chemistry, charge transfer and energy transfer processes, 8A34
   radiolysis, effects of density, 7-5, 7-6
   reaction rate studies by electron paramagnetic resonance, 5B17
   statistical mechanics of dense, 6-7
   study of ions in, 7-18
   as thermodynamic working fluids, physical chemistry of, 8C11
Geochemistry
   importance of radioisotope half-lives and decay schemes, 2A21
   nuclear applications to, 3A3
Geology
   thorium recovery from common rocks, 8D11
Germane
      (See Germanium hydrides)
Germanium
   lithium-drifted semiconductor detectors, 5A38
Germanium compounds
   disproportionation, 7-36
Germanium, diphenyl-2-butene complex
   structure, 1A11
Germanium hydride ions (GeH_3BH_3)
   preparation, 5B8
Germanium hydrides
   reaction with borohydride ion, 5B8
Glass
      (See also Organic glasses)
   ancient, analytical studies at BNL, 3A13
Glass spheres
   fluidization, use to study liquid kinetics, 5A63
Glutamic acid
   metal complexes, infrared spectra, 7-39
Glycine
   complexes with transition metals, 7-39
Glycols
   diastereoisomers, identification by nuclear magnetic resonance, 8A29
Gold
   electronic configuration, Mossbauer effect studies, 5A48
   nuclear magnetic field studies, 5A47
Gold-197
   (p, $p\pi^+$) reaction, 2A13
Gold-199
   search for, 2A27
Gold-200
   search for, 2A27
Granite
   thorium recovery, geologic aspects, 8D11
   thorium and uranium content, survey, 8D10
Graphite
   hydrogen reaction with, 5B21
   sublimation curves, experimental determination, 3B2
Gravimetry, thermo-
      (See Thermogravimetry)
Hafnium
   corrosion and film studies in hydrogen fluoride solution, 8A18
   energy levels in the rotational region, 5A35
   neutron diffraction studies, 2A74
Hafnium borides (HfB_2)
   enthalpy of formation, 2B10
Hafnium fluorides (HfF_4)
   enthalpy of formation, 2B10
Hafnium systems ($Hf-HfI_4$)
   physical and chemical properties, 1A19
Hafnium systems (Hf-S)
   phase relations at high temperature, 1A21
Half life
   cerium-130, 5A6
   praseodymium-130, 5A6
   praseodymium-132, 5A6
   praseodymium-134, 5A6
Halides
      (See also specific halide compounds)
   amine complexes, dissociation in solution, 7-30
   flash spectroscopy at cryogenic temperatures, 6-5
   of metals, physical and chemical properties of reduced, 1A19
   physico-chemical characterization by mass spectrometry, 1A17
Hall coefficients
   of lanthanum iodides, 1A19
Halogen fluorides
   solvent use in xenon fluoride studies, 2A67
Halogens
   alkali atom beams, collisions, 8A20
   surface reactions with nickel, 6-1
Hamiltonian equations
   computer calculations, 2A69
   rate process studies using digital computers, 5A7
Hammet Activity Function
   organophosphorus compounds, 2A88
Heat
   effects on fluorocarbons, 3B3
Heat capacity
   determination of magnetic properties by, 1A12
   liquid helium-3 at low temperatures, 2A79
   low temperature calorimetric studies, 2A80
   transition elements and compounds, measurement, 8A11
Heat of formation
   intermetallic compounds in binary liquid metal solutions, 2B3
   transition element compounds, measurement, 8A11
Heat of solution
   rare gases in liquid alkali metals, 2B1
   transition element compounds, measurement, 8A11
Heat transfer
   between immiscible fluids, 5A74
   in chemical equipment, turbulent, 1B7
   for fluids, mathematical studies, 1B3
   measurement of transport parameters, thermodynamic studies of data, 5B28
Heavy Ion Linear Accelerator
   platinum isotope preparation by irradiation of rare

    earths, 5A11
  praseodymium neutron deficient isotope studies, 5A6
Heavy ions
  fission induction, fission cross section studies, 5A21
  fission induction, measurement of kinetic energy of fission fragments, 5A20
  reactions, in-beam spectroscopy, 5A35
Heavy water
  (See Water(D_2O))
Helium
  diffusion studies, 8C11
  modulated atomic beams, interaction with heated surfaces, 8A21
  sparging of rare gases from liquid alkali metals by, 2B1
Helium-3
  nuclear reaction studies, 2A1
  nuclear reactions, activation analysis by, 5A57
  nuclear reactions, mechanism of low-energy, 5A29
Helium-3 (liquid)
  properties at low temperatures, 2A79
Helium-4
  nuclear reactions, mechanisms of low-energy, 5A29
  proton scattering and polarization at high energy, 5A26
Helium-4 (liquid)
  properties at low temperatures, 2A79
Helium ions
  (See also Alpha particles)
  bombardment of targets in studies of nuclear reactions, 5A24
  fission reaction studies with, 2A19
Heptane
  molecular complexity of organo-phosphorus compounds in, 2A86
Hexamine cobalt complexes
  gamma radiation, chemical effects, 1A22
Hexane
  radiation chemistry of, 3A5
  recoil chemistry of carbon-11, 1A29
High Flux Beam Reactor
  neutron source in diffraction studies of magnetic materials, 3A12
High-temperature chemistry
  bonding studies of solids, liquids, and gases, 2A54
  condensed-phase relations, 1A21
  electrochemical and spectroscopic studies, 3B1
  fundamental studies, 7X1
  laser studies, 2A53
  metal interactions with molten halides, 1A20
  molten salts, 4-1
  phase studies, 2A56
  rate process studies, 2A55
  surface ionization studies, 2A53
High-temperature facilities
  x-ray diffraction studies, 2A71
HILAC
  (See Heavy Ion Linear Accelerator)
Holmium
  absorption spectra in oxy-acetylene flames containing ethanol solutions of perchlorates, 1A8
  bombardment by oxygen-16 ions to produce rhenium-181, 5A21
Holmium-165
  coulomb excitation studies using heavy ions, 5A36
Holmium intermetallic compounds ($HoGa_2$)
  neutron diffraction studies, 3A12
Holmium oxides (Ho_2O_3)
  phase studies at high temperatures and pressures, 2A56
Horseshoe crab
  nucleic acid changes during learning, 3A11
Hydration
  metal ions, kinetic and stoichiometric studies, 5B6
Hydration numbers
  for alkali cations, 3B5
Hydrazine
  formation from ammonia, radiation induced, 5B23
Hydrides
  (See also Deuterides)
  isotope effects of deuterium, 1A9
  low temperature calorimetric studies, 2A80
  mixed, stereochemistry in reduction of organic compounds by, 7-28
  physico-chemical characterization by mass spectrometry, 1A17
Hydrocarbons
  (See also Aliphatic compounds, Aromatic compounds, and Organic compounds)
  decomposition on metal surfaces, kinetic studies, 1A16
  graphite deposition from, 3B2
  ionization in the gas phase, 7-18
  luminescence from gamma-irradiation, 7-11
  molar volumes, isotope effects, 1A9
  molecules, collisions with high-energy protons, 2A38
  nitration of aromatic in vapor phase, 5A61
  pyrolysis, effect of oxygen, 5A75
  radiation-induced reactions, 3B7
  radiolysis, 7X2
  radiolysis, ionic reactions, 6-2
  reaction with nitric acid in solvent extraction systems, 8A31
Hydrochloric acid
  reaction with sulfur-nitrogen compounds, 5B7
Hydrogen
  abstraction reactions of trifluoromethyl radical deuterium kinetic effects, 3A7
  bond strength studies in bidentate ligands, 2A82
  bonding in acidic organophosphorus compounds, 2A87
  π complexes, 8A28
  determination in submilligram samples of organic compounds, 5A71
  effects on extraction effectiveness of organophosphorus compounds, 2A88
  effect of extraction of rare earths by organophosphorus compounds, 2A89
  effect on molecular complexity of organophosphorus compounds in solutions, 2A86
  isotopic mixtures, scattering cross sections, 8A21
  permeation rate through metal membranes, 2B6
  reaction with free radicals, electron paramagnetic resonance studies, 5B17
  reactions on hot graphite surface, 3B21
  use as reducing agent for removal of oxygen from liquid metals, 5A66
Hydrogen (liquid)
  molal volume correlation with zero-point energy, 3A7
Hydrogen atoms
  reaction rates with aromatic rings, 7X2
Hydrogen fluoride
  solvent use in xenon fluoride ionization studies, 2A66
  solvent use in xenon fluoride studies, 2A67
  thermodynamic properties, determination, 6-6
  zirconium corrosion in, 8A18
Hydrogen free radicals
  reaction rate studies by electron paramagnetic resonance, 5B17
Hydrogen ions
  interaction with 1,10-phenanthroline in aqueous solution, 1A1
  reduction kinetics, 8C4
  in solvent extraction, 4-2

  - solvation, solvent extraction studies, 5A50
  - transfer reactions in radiolysis, 6-2
- Hydrogen isotopes
  - (See also Deuterium and Tritium)
  - analysis by mass spectrometry, 5A13
- Hydrogen peroxide
  - decomposition, stored-energy effects on platinum catalyst, 7-21
  - irradiated single crystals, paramagnetic resonance spectroscopy, 8A10
- Hydrogen resonance lamps
  - development, 6-3
- Hydrogen sulfide
  - reactions with nitrogen, 5B7
- Hydrogen systems (CO-HD)
  - energy transfer in ion-molecule interactions of, 3A10
- Hydrogen systems (CO_2-HD)
  - energy transfer in ion-molecule interactions of, 3A10
- Hydrogen systems (HD-N_2)
  - energy transfer in ion-molecule, interactions of, 3A10
- Hydrogen systems (HD-N_2O)
  - energy transfer in ion-molecule interactions of, 3A10
- Hydrogen systems (HD-O_2)
  - energy transfer in ion-molecule, interactions of, 3A10
- β-Hydro juglone
  - (See Juglone, β-hydro-)
- Hydrolysis
  - of cerium, 3B8
  - enzyme substrates by methanol solutions at low temperatures, 3A11
  - inorganic ions, studies on, 8A12
  - metallic cations at high temperature, 8C5
  - olefins, as carbonium ion prototype reaction, 3A9
  - radon fluorides, 2A58
  - rare gas type cations, 2A81
  - xenon fluorides in acidic and alkaline solutions, 5A49
  - xenon fluorides, properties of, 2A66
- β-Hydronaphthazarin
  - (See Napththazarin, beta-hydro-)
- β-Hydronaphthazarin disulfonate
  - (See Naphthazarin disulfonate, beta-hydro-)
- di-β-Hydronaphthazarin
  - (See Naphthazarin, di-beta-hydro-)
- Hydronium ion
  - hydration, solvent extraction studies, 5A50
- Hydroperoxy radical
  - absorption spectra in irradiated oxygenated water, 2A45
- Hydrophosphorous acid
  - complexes with chromium ions, 1A15
- Hydrous oxides
  - ion exchange and adsorption properties, 8A23
- Hydroxamic acids
  - ion exchange properties, 8A31
- Hydroxide ions
  - substitution rates in platinum complexes, 1A24
- Hydroxycarboxylic acids
  - complexes with rare earths, 1A27
- Hydroxyl group
  - absorption in water, 2A44
  - effects on extraction effectiveness of organophosphorus compounds, 2A88
  - effect of extraction of rare earths by organophosphorus compounds, 2A89
  - effect on molecular complexity of organophosphorus compounds in solutions, 2A86
  - reaction rate constant studies using pulsed irradiation techniques, 2A42
  - solvation, solvent extraction studies, 5A50
- Hyperfine structure
  - elements from radium through curium, 2A72
  - erbium-165, 5A13
  - mass spectrometry studies, 5A13
  - promethium-148, 5A13
  - rhenium isotopes, 5A13
  - tungsten isotopes, 5A13
- Hypophosphite ions
  - complexes with chromium ions, 1A15
- Ice
  - irradiated single crystals, paramagnetic resonance spectroscopy, 8A10
- Indium-115
  - decay constants, 2A21
- Indium alloys (In-U)(liquid)
  - thermodynamic properties, 2B3
- Inert gases
  - (See Rare gases)
- Infrared radiation
  - studies of thoria gel, 8D14
- Infrared spectra
  - (See Spectra (infrared))
- Inorganic compounds
  - adsorption on, 8A23
  - bacterial conversion studies, 5A69
  - crystallography studies, 3A12
  - interaction with organic solvents, 4-2
  - oxidation-reduction studies, 3A8
  - physico-chemical characterization by mass spectrometry, 1A17, 1A18
- Instruments
  - (See also specific instruments, e.g., Scintillation detectors)
  - calorimeter development for determination of uranium-235m decay energy, 5A12
  - for chemical analysis, development, 8B3
  - design and development for nuclear chemistry, 5A40
  - detector for species in gas-phase reactions, 5B26
  - determination of radiative lifetime of excited electronic states, 5B3
  - external field polarization device for nuclear orientation, 5A2
  - high precision drop type calorimeter development, 2B13
  - magnetic susceptibility determination, 2B5
  - multiparameter pulse-height analyzer, 8A6
  - neutron diffractometer modifications, 2A74
  - semiconductor radiation detector studies, 5A38
- Insulation (thermal)
  - pressure effects on thermal conductivity, 5B12
- Interfaces
  - between electrolytes, electrochemical properties, 6-9
  - of liquids, studies by oscillating jets, 5A62
- Intermetallic compounds
  - (See also by name of constituent metals e.g., Cadmium intermetallic compounds (UCd_{11}), etc.)
  - neutron diffraction studies, 3A12
  - phase studies of effusion method, 2B4
  - solubility in fused salts, 2B8
  - thermodynamic properties in binary liquid metal solutions, 2B3
- Internal conversion
  - high precision measurements, nuclear level studies, 5A4
  - nuclear structure studies, 5A3
- Iodates
  - spectral studies, 2A87
- Iodides
  - solvent extraction of alkali cations, 3B5
- Iodine
  - determination of radiative lifetime in excited state, 5B3
  - muon reactions, radiochemical studies, 2A12
- Iodine-129

- decay constants, 2A21
- Iodine ion
  - reaction rate with xenon trioxide in acidic solution, 5A49
- Ion exchange
  - actinide elements, 2A60
  - alkali metals, isotope separation by, 8A27
  - analytical separations by, 1A5
  - basic studies with various solvents, 5A50
  - corrosion inhibitors, surface effects, 8A16
  - development of new processes, 8D8
  - heavy element separation techniques, 5A5
  - of inorganic materials, 8A23
  - inorganic systems in radiochemistry, 8D8
  - isotope separation by, 1A26
  - liquid ion exchangers, basic studies, 5A50
  - physical chemical studies of synthetic organic systems, 8A14
  - process development, 8A15
  - process development for chemical separations, 8D1
  - protactinium solution studies, 8D9
  - rare earth separations by, 1A25
  - resin stability in chemical and radiation environments, 8D8
  - separation of transplutonium elements, use of zirconium phosphate gels, 2A90
  - separations by, process research, 8A15
  - solvent exchange studies, 4-2
- Ion sources
  - design for positive-negative mass spectrometers, 1A18
- Ionization
  - photosensitized, 5B15
  - rare gases, experimental threshold laws by mass spectrometry, 2A85
- Ionization potentials
  - measurements by surface ionization studies, 5A51
- Ionized gases
  - charge neutralization rates, 5B14
- Ions
  - (See also <u>Anions</u>, <u>Cations</u>, <u>Heavy ions</u>, and specific ions by name e.g., <u>Oxygen-16 ions</u>, <u>Neon-22 ions</u>, etc.)
  - configuration interactions, 5A43
  - detection instrument for chemical reactions, 3B7
  - diffusion rates in ion exchangers, 8A14
  - excitation and fragmentation studies, 7-15
  - formation in organic glassy systems by gamma irradiation, 7-16
  - formation by photon interactions, 6-4
  - formation in solvent extraction, 4-2
  - high energy, collisions with isolated molecule, 2A38
  - interactions with ions, theoretical studies, 2A81
  - interaction with molecules in gaseous phase, 3A10
  - interactions with water, theoretical studies, 2A81
  - metal, fluorometric determination, 7-38
  - metal, kinetic and stoichiometric studies of hydration, 5B6
  - multiply charged, formation by electron impact, 5A45
  - range-energy relationship in matter, 5A23
  - rare earths, theoretical studies of spectra, 2A76
  - reaction rate with xenon trioxide and sodium xenate in aqueous solutions, 5A49
  - reactions in charged-particle tracks, 7-19
  - reactions, mass spectrometry studies, 8A34
  - reactions in radiation chemistry, 6-2
  - role in liquid organic reactions, 3B7
  - role in radiation chemistry of organic systems, 5A59
  - solvation, solvent extraction studies, 5A50
  - study in the gas phase, 7-18
- Iridium fluorides (IrF_6)
  - quantum mechanical studies of electronic-nuclear interactions, 2A75
- Iron
  - chronopotentiometry in molten fluorides, 8B2
  - corrosion inhibition by adsorption of benzoate ions, 8A17
  - phase studies at high pressure, 5B11
  - removal from refractory metals, 5B2
  - separations by reversed-phase chromatography, 1A4
  - solvent extraction from acid solutions by amines, 8D3
- Iron-52
  - production of pure, 3B10
- Iron-55
  - internal-conversion electron spectra studies, 2A23
- Iron-57
  - Mossbauer effect under high pressure, 5B13
- Iron alloys
  - fluorometric determination, preliminary separations in, 7-38
- Iron ions
  - oxidation by cobalt ions in presence of chloride ions, 3A8
- Iron oxide systems (Fe_2O_3-MgO)
  - diffusion studies, 7-24
- Iron oxide systems (Fe_2O_3-NiO)
  - diffusion studies, 7-24
- Iron oxide systems (Fe_2O_3-ZnO)
  - diffusion studies, 7-24
- Iron uranates
  - crystal structure, x-ray diffraction studies, 2A71
  - uranium-oxygen bond studies, 2A78
- Irradiation facility
  - isotopic neutron source development, 2A33
- Isobutyric acid, amino-
  - complexes with transition metals, 7-39
- Isomerization reactions
  - of trialkylboranes, kinetics and equilibria, 7-32
- Isomers
  - cross-section ratio studies, 2A3
  - identification by nuclear magnetic resonance spectroscopy, 8A29
- Isopiestic studies
  - of aqueous salt solutions at high temperature, 8C8
- Isotope effects
  - chemical processes, 3A7
  - chemical reactions, 8A27
  - chemical reactions, 8A28
  - deuterium in 3,4-furandicarboxylic acid, 1A11
  - deuterium in hydrides, 1A9
  - in free-radical aromatic substitution, 7-27
  - of molecules, spectroscopic studies, 8A26
  - physical processes, 3A7
- Isotope shift
  - elements from radium through curium, 2A72
- Isotopes
  - abundance, mass spectrometry measurements, 8A22
  - production from triton interactions, 3B10
  - separation by ion exchange, 1A26
  - separation by exchange chemistry, 8A27
  - separation techniques for heavy elements, 5A5
  - separation, isotope effects studies, 3A7
- Isovaline
  - complexes with transition metals, 7-39
- Jahn-Teller effect
  - hexafluoride molecules, 2A75
- Juglone, β-hydro-
  - chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
- Ketones
  - (See also specific ketones by name, e.g., <u>Methyl isobutyl ketone</u>)

  formation, isotope effects, 8A28
  molecular complexity of organo-phosphorus compounds in, 2A86
Kinetic energy
  fission fragments, measurement in heavy-ion-induced fission, 5A20
Kinetic studies
  chlorination rate of uranium tetrachloride in fused salts, 5B18
  diffusion-controlled oxidation of refractory metals, 5B20
  electrodes in regenerative cells, 2B9
  isotope effects on reaction rates, 3A7
  liquid metal extraction, 5B19
  oxidation-reduction reactions, 3A8
  reaction rates of gaseous free radicals, electron paramagnetic resonance studies, 5B17
Kinetic theory
  of liquids, study using fluidized glass spheres, 5A63
  of polyatomic molecules, 8C11
Krypton
  compounds with fluorine, radiation chemistry, 3B3
  thermodynamic properties, determination from solubility in liquid alkali metals, 2B1
Krypton-85
  surface area determination by, 3B2
Krypton fluorides
  synthesis, 2A66
Krypton fluorides (KrF_2)
  mass spectrometry, 2A68
Krypton resonance lamps
  development, 6-3
Lactic acid dehydrogenase
  reactions at low temperatures, 3A11
Lamps
  atomic resonance type, 6-3
Lanthanide rare earths
    (See Rare earths (lanthanides))
Lanthanum-135
  energy-level diagrams, 8A8
Lanthanum alloys (Cd-La)(liquid)
  phase studies, 2B4
  thermodynamic properties, 2B3
Lanthanum alloys (La-Zn)(liquid)
  phase studies, 2B4
Lanthanum chlorides ($LaCl_3$)
  actinide doping, fluorescence, 5A55
  paramagnetic resonance of actinide ions in, 5A52
Lanthanum halides
  electronic conductivity of metal solutions, 1A20
Lanthanum iodides
  magnetic susceptibility measurements, 1A19
Lanthanum oxides
  ion exchange properties, 8A23
Lanthanum oxides (LaO)
  absorption coefficient measurement, 5B5
  determination of radiative lifetime in excited state, 5B3
Lanthanum potassium nitrates
    (See Potassium lanthanum nitrates)
Lasers
    (See also Optical pumping)
  application to radiation chemistry, 7-14
  coherence properties of beam in helium neon type, 5A73
  divalent actinide element studies, 2A61
  high temperature chemistry use, 2A53
  light source use in Raman spectroscopy of xenon hexafluoride, 2A66
  light source use in Raman spectroscopy of yellow solutions, 2A67
Lead
  analysis in meteorites, 2A29
Lead-107
  half-life determination, 2A21
Lead-208
  nuclei near to, decay schemes of, 5A7
  nuclei near to, nuclear spectroscopy of, 5A8
Lead alloys
  solubility in fused salts, 2B8
Lead alloys (Pb-U)(liquid)
  thermodynamic properties, 2B3
Lead alloys (Bi-Pb)
  cadmium separation by extraction with a fused salt, 1B2
Lead ions
  absorption spectra of hydrated electrons in aqueous solutions of, 2A43
Lead, tetraethyl-
  radiation and photochemistry in benzene and cyclohexane, 7-7
Learning
  biochemical studies of planaria, tracer use, 3A11
LET
    (See Linear energy transfer)
Leucine
  metal complexes, infrared spectra, 7-39
Lewis acids
  strength measurements by proton magnetic resonance, 7-34
Lewis bases
  strength measurements by proton magnetic resonance, 7-34
Light
  fluorescence excitation of rare earths, 2A61
Linear energy transfer
  effects on radiolysis, 8A33
  effects on radiolysis, 8A34
Liquid-liquid settlers
  design, 5A68
Liquid metals
    (See Metals (liquid))
Liquids
  diffusion coefficient measurements, 7-26
  interfaces, studies with oscillating jet, 5A64
  kinetic studies using fluidized glass spheres, 5A63
  radiation chemical studies, 8A34
  structure, x-ray and neutron diffraction studies, 8A24
  turbulent heat and mass transport in plant equipment, 1B7
Lithium-6
  enrichment by ion exchange, 1A26
  ratio with lithium-7 in compounds ionized from hot filaments, 2A53
Lithium-7
  ratio with lithium-6 in compounds ionized from hot filaments, 2A53
Lithium-9
  formation cross sections, 3A1
Lithium alloys (Bi-Li)
  spectrophotometry in fused salt solutions, 2B8
  solubility in lithium chloride - lithium fluoride systems, 2B8
  thermodynamic properties, regenerative cell studies, 2B7
Lithium alloys (Li-Sn)
  thermodynamic properties, regenerative cell studies, 2B7
Lithium alloys (Li-Te)
  spectrophotometry in fused salt solutions, 2B8
Lithium aluminum hydride
  stereochemistry in reduction of organic compounds by, 7-28
Lithium bromides
  molecular beam electric resonance spectroscopy, 5A46

- Lithium bromide systems (LiBr-LiH)
  - phase studies, 2B6
- Lithium carbides (Li_2C_2)
  - neutron diffraction studies, 2A74
- Lithium chlorate (liquid)
  - rare earth oxide preparation in, 2A62
- Lithium chloride systems (KCl-LiCl)(liquid)
  - solvent use in rare earth absorption spectra studies, 2A61
- Lithium chloride systems (KCl-LiCl-UCl_4)(liquid)
  - chlorination rate of uranium tetrachloride in, 5B18
- Lithium chloride systems (LiCl-LiF-LiH)
  - phase studies, 2B6
- Lithium chloride systems (LiCl-LiH)
  - phase studies, 2B6
- Lithium fluoride systems (LiCl-LiF-LiH)
  - phase studies, 2B6
- Lithium fluorides
  - molecular beam electric resonance spectroscopy, 5A46
  - radiolysis, 8C2
- Lithium hydride
  - regenerative cell studies, 2B6
- Lithium hydride systems (LiBr-LiH)
  - phase studies, 2B6
- Lithium hydride systems (LiCl-LiH)
  - phase studies, regenerative cell studies, 2B6
- Lithium hydride systems (LiCl-LiF-LiH)
  - phase studies, 2B6
- Lithium hydride systems (LiH-NaCl)
  - phase studies, 2B6
- Lithium hydrogen carbides ($LiHC_2$)
  - neutron diffraction studies, 2A74
- Lithium hydroxide monohydrate
  - neutron diffraction studies of structure, 8A35
- Lithium iodides
  - molecular beam electric resonance spectroscopy, 5A46
- Lithium ions
  - nuclear reactions, 2A1
- Lithium nitrate systems (KNO_3-$LiNO_3$)(liquid)
  - potentiometric studies, 3B9
  - *rare earth oxide preparation in*, 2A62
  - solvent use in rare earth absorption spectra studies, 2A61
  - solvent use in rare earth excited state studies, 2A62
- Lithium sulfate
  - solubility in water at high temperature, 8C7
- Lithium uranates
  - crystal structure, x-ray diffraction studies, 2A71
- Low-temperature research
  - calorimetry, 5B24
  - x-ray diffraction studies, 2A71
- Luminescence
  - *(See also Fluorescence and Phosphorescence)*
  - decay-time measurements, 7-10
  - *decay-time studies*, 7-13
  - energy-transfer studies, 7-13
  - *of hydrocarbons from gamma radiation*, 7-11
  - quenchers, efficiencies of metal alkyls, 7-7
  - *in organic materials, energy transfer studies*, 7-8
- Lutetium
  - isolation by ion exchange, 1A25
- Lutetium-175
  - coulomb excitation studies using heavy ions, 5A36
- Lutetium-176
  - half-life and beta spectrum, 2A21
- Lutetium oxides (Lu_2O_3)
  - phase studies at high temperatures and pressures, 2A56
- Magnesium
  - isotope exchange reactions, 8A27
- Magnesium (liquid)
  - liquid metal extraction studies using, 5B19
- Magnesium-22
  - (p,t) reaction, nuclear energy level studies, 5A27
- Magnesium-28
  - production by triton interaction, 3B10
- Magnesium carbides (MgC_2)
  - neutron diffraction studies, 2A74
- Magnesium carbides (Mg_2C_3)
  - neutron diffraction studies, 2A74
- Magnesium chloride
  - absorption coefficient measurement, 5B5
- Magnesium oxide
  - ion exchange properties, 8A23
  - stresses produced by oxygen adsorption, 7-23
- Magnesium oxide systems (Fe_2O_3-MgO)
  - diffusion studies, 7-24
- Magnesium oxide systems (MgO-NiO)
  - diffusion studies, 7-24
- Magnetic fields
  - nuclear polarization studies, 5A2
- Magnetic materials
  - electrostatic field effects, 2A74
  - induced internal fields in ferromagnets, 5A47
  - neutron diffraction studies, 2A74
  - structure, neutron diffraction studies, 3A12
- Magnetic moments
  - mercury-203, studies using optical pumping, 5A72
  - praseodymium-142, 5A13
  - rhenium isotopes, 5A13
  - spherical nuclei, theoretical calculation comparison with experiment, 5A15
- Magnetic ordering
  - studies with organic free radicals, 1A14
- Magnetic resonance
  - (See Electron paramagnetic resonance, Nuclear magnetic resonance, and Proton magnetic resonance)
- Magnetic susceptibility
  - actinide sulfides, 2A83
  - *apparatus for determination*, 2B5
  - of metal halides, measurement, 1A19
  - rhenium hexafluoride, 2A83
  - thorium monosulfide - uranium monosulfide solid *solutions*, 2B5
  - uranium - cadmium intermetallic compounds, 2A83
  - uranium monosulfide, 2B5
  - xenon hexafluoride, 2A83
- *Magnetism*
  - (See also Antiferromagnetism, Ferromagnetism, and Paramagnetism)
  - mechanism, nuclear magnetic field studies, 5A47
  - *in solids, fundamental studies*, 1A12
- Manganese-53
  - *half-life measurement*, 2A27
- Manganese-55
  - *proton reactions*, 2A4
- Manganese, cyclheptatrienyl-cyclopentadienyl-
  - structure, 1A11
- Manganese halides
  - complexes with aryl amines, dissociation in solution, 7-30
- Manganese intermetallic compounds ($ErMn_2$)
  - neutron diffraction studies, 3A12
- Manganese intermetallic compounds ($TmMn_2$)
  - neutron diffraction studies, 3A12
- Manganese uranates
  - crystal structure, x-ray diffraction studies, 2A71
  - uranium-oxygen bond studies, 2A78
- Mass
  - fission fragments, precise determination of, 5A17
- Mass spectrometers

(See Spectrometers (mass))
Mass transfer
  between immiscible fluids, 5A74
  from changing droplets in solvent extraction columns, 1B1
  in chemical equipment, turbulent, 1B7
  effects on current distribution on rough surfaces, electrochemical studies, 5B29
  in gas-liquid equipment, 5A67
  in gas-liquid systems, 5A76
  measurement of transport parameters, thermodynamic studies of data, 5B28
  regenerative cell kinetics studies, 2B9
  turbulent effects between fluids and a wall, 5A70
Mathematics
  assymetric rotor nuclear model studies, 2A77
  of fluid heat transfer, 1B3
  ionization intensity function calculation for rare gases, 2A85
  nuclear reaction theoretical calculations, 2A70
  nuclear shell model calculations, 5A14
  nuclear structure calculations, 5A15
  quantum mechanical studies of electronic-nuclear interactions, 2A75
  theoretical nuclear chemistry calculations, 2A69
Membranes
  metal, hydrogen permeation rates, 2B6
Mercaptans
  oxidation in solutions, free radical formation, 1A14
Mercury
  hanging-drop electrodes, use in fused salt studies, 3B9
  nuclear studies in the vibrational region, 5A35
  optical pumping experiments, 5A72
Mercury-203
  nuclear magnetic moment measurement, polarization by optical pumping, 5A72
Mercury alloys
  (See Amalgams)
Mercury chloride systems ($HgCl_2$-$Hg(SCN)_2$)
  equilibria, 3A8
Mercury thiocyanate systems ($HgCl_2$-$Hg(SCN)_2$)
  equilibria, 3A8
Mercury thiocyanates ($Hg(SCN)_2$)
  aggregation state in water, 3A8
Meso- isomers
  identification by nuclear magnetic resonance spectroscopy, 8A29
Metal alkyls
  efficiency as luminescence quenchers, 7-7
Metal halides
  amine complexes, dissociation in solution, 7-30
  thermodynamic data compilation, 5B2
Metal ions
  fluorometric determination, 7-38
  interaction with anions, spectral studies, 2A65
Metal nitrates
  solvent extraction from acid solutions by amines, 8D3
Metal oxides
  spinel formation in, 7-24
  stresses produced by oxygen adsorption, 7-23
  thermodynamic data compilation, 5B2
Metals
  (See also Alloys and specific metals by name)
  complexing by ligands, water exchange rate studies, 5B6
  corrosion inhibition by adsorption of organic ions, 8A17
  heat capacity measurements at low temperatures, 5B24
  interstitial oxygen and nitrogen determination, 1A6
  molten halide solutions, spectrophotometry and chronopotentiometry, 3B1
  molten salt solutions, 8A25
  oxygen determination in low-boiling, 2A36
  passive surfaces, ion exchange properties, 8A16
  phase diagrams, 5B1
  phase studies at high pressure, 5B11
  reaction with their molten halides, 1A20
  surface ionization studies, 5A51
  surface reactions, kinetic studies of hydrocarbon decomposition, 1A16
  reactions with their molten halides, 1A19
  thermodynamic property determination at high pressure, 5B10
  transplutonium, preparation and properties, 5A54
Metals (liquid)
  alloys, thermodynamic properties, 5A62
  bimetallic regenerative cell studies, 2B7
  bimetallic regenerative cell studies, 2B8
  chemical properties at high temperature, 7X1
  container materials for distillation, 1B6
  distillation studies, 1B6
  extraction kinetics, 5B19
  fused-salt extraction, 1B2
  heat transfer, mathematical studies, 1B3
  oxygen removal by hydrogen, 5A66
  phase studies of binary solutions, 2B4
  solubility of rare gases in, 2B1
  thermodynamic properties, 1B4
  thermodynamic properties of binary solutions, 2B3
  vaporization studies, 1B5
Metastable states
  of molecules, formation by electron impact, 5A44, 5A45
Meteorites
  analysis, 2A29
  analysis, 2A30
  analytical studies at BNL, 3A13
  nuclear chemistry studies, 3A3
  silver elemental and isotopic abundances, 2A27
Methane
  deuterated, infrared spectroscopy, 6-8
  diffusion coefficient in dilute solutions, 7-26
  ions, structure, 7-15
  radiolysis, CH_2 production, 6-2
  radiolysis, phase effects, 8A34
Methane, dibenzoyl-
  structure, 1A11
Methane, phenylazotriphenyl-
  reaction with benzene-d_1, isotope effects, 7-27
Methane, tetrafluoro-
  (See Carbon tetrafluoride)
Methane, tetranitro-
  (See Tetranitromethane)
Methane, trifluoro-
  isotopic analysis for hydrogen, isotope kinetics studies, 3A7
Methanol
  solvated electron absorption spectra, 2A41
  solvent, spectrophotometry, 8A19
Methyl astatine
  identification, 2A59
Methyl ether
  complexes with boron trifluoride, isotope effects on Raman and infrared spectra, 8A26
Methyl isobutyl ketone
  molecular complexity of organo-phosphorus compounds in, 2A86
3-Methylpentane
  (See Pentane, 3-methyl-)
Methyl pyridines
  (See Pyridines, methyl-)
Methyl radical, trifluoro-
  (See Trifluoromethyl radical)

- Methyl radical, tris di-t-butyl p-phenoxy-
  - structural studies by x-ray diffraction, 3A9
- Methyl radicals
  - ions, structure, 7-15
- Methylene
  - hot-atom chemistry, 3A6
- Methylene blue perchlorate
  - solvent extraction, 3A8
- Mica
  - use for fission-fragment detection, 5A40
- Milking systems
  - for radioisotopes, development, 3B10
- Mixer settlers
  - design of liquid-liquid, 5A68
  - development for solvent extraction, 8D4
- Models
  - liquid kinetic studies using fluidized glass spheres, 5A63
- Molds
  - growth in heavy water, 2A50
- Molecular beams
  - alkali atom interactions with halogens, 8A20
  - electric resonance spectroscopy, 5A46
  - of hydrogen, reactions with graphite, 5B21
  - modulated interactions with heated surfaces, 8A21
- Molecular diffusion
  - mass transfer from droplets in solvent extraction, 1B1
- Molecular structure
  - xenon hexafluoride, theoretical studies, 2A66
- Molecular weights
  - measurement on polymers, 8C1
- Molecules
  - absorption spectra, 1A8
  - deuterated, infrared spectroscopy and molecular constants, 6-8
  - diffusion coefficients, measurement, 7-26
  - electron impact studies, 7-15
  - excited, energy transfer studies, 7-2
  - excited, reactions in radiation chemistry, 6-2
  - excited, study by vacuum ultraviolet photochemistry, 6-3
  - of gases, structure studies by electron diffraction, 1A9
  - high-energy ion collisions of isolated, 2A38
  - interaction with ions in gaseous phase, 3A10
  - interactions, 8C11
  - interactions in molten salts, 4-1
  - interactions in solvent extraction, 4-2
  - isotope effects, spectroscopic studies, 8A26
  - metastable electronic states, formation by electron impact, 5A44, 5A45
  - motions, effects of electronic interactions, 7-20
  - polyatomic, kinetic theory of, 8C11
  - quantum mechanics of unstable, 6-7
  - reactions with atoms in crossed-beam studies, 2A39
  - structure, nuclear magnetic resonance studies, 5B25
- Molten metals
  - (See Metals (liquid))
- Molten salts
  - (See Fused salts)
- Molybdates
  - ion exchange and adsorption properties, 8A23
- Molybdenum
  - calorimetric studies, 2B13
  - diffusion-controlled oxidation, 5B20
  - separations by hydrogen peroxide elution, 1A5
  - separations by reversed-phase chromatography, 1A4
  - solvent extraction from acid solution by amines, 8D3
  - surface reactions with chlorine, 6-1
- Molybdenum compounds
  - thermodynamic data compilation, 5B2
- Molybdenum fluorides (MoF_6)
  - low temperature calorimetric studies, 2A80
- Molybdenum ions
  - hydrolysis studies, 8A12
- Momentum transport
  - in chemical equipment, turbulent, 1B7
- Monel
  - use in nitrofluor process, 3B4
- Monte Carlo calculations
  - extension to higher energies, 3A1
- Moon
  - surface analysis by Rutherford scattering measurements, 2A28
- Mossbauer effect
  - gamma ray energy measurements, 5A48
  - high-pressure studies, 5B13
  - impurity atoms in magnetic materials, 5A47
  - in tin complexes, 7-29
- Mott scattering
  - beta polarization studies, 8A4
- Muon-capture reactions
  - radiochemical studies, 2A12
- Naphthadiquinone
  - (See Diquinone, naphtha-)
- Naphthalene, perfluoro-
  - radiation and heat, effects on, 3B3
- Naphthalene, 1,4,5,8-tetrahydro-
  - chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
- Naphthazarin
  - chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
- Naphthazarin, beta-hydro-
  - chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
- Naphthazarin, di-beta-hydro-
  - chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
- Naphthazarin disulfonate, beta-hydro-
  - chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
- Neodymium
  - ionization-potential measurement by surface ionization, 5A51
- Neodymium alloys (Cd-Nd)(liquid)
  - phase studies, 2B4
- Neodymium alloys (Nd-Zn)(liquid)
  - phase studies, 2B4
- Neon
  - diffusion studies, 8C11
  - optical pumping experiments, 5A72
- Neon-17
  - production, 2A1
- Neon-23
  - radioactive decay studies, 8A5
- Neon-20 ions
  - irradiation of rare earths for platinum isotope production, 5A11
- Neon-22 ions
  - bombardment of terbium to produce rhenium-181, 5A21
- Neptunates
  - preparation in fused salt solutions, 2A62
- Neptunium
  - emission spectroscopy, 2A72
  - irradiation with helium ions and deuterons, 2A1
- Neptunium-236
  - production and properties, 2A22
- Neptunium compounds
  - low temperature calorimetric studies, 2A80
- Neptunium fluorides (NpF_6)
  - low temperature calorimetric studies, 2A80

Neptunium oxides
  preparation in fused salt solutions, 2A62
Neptunium oxides (NpO_2)
  high temperature properties, 2A60
Neptunium oxides (Np_2O_5)
  preparation, 2A60
Neptunium oxides (NpO_3)
  preparation, 2A60
Nervous system
  biochemical studies of lower animals, 3A11
Neutrinos
  from the sun, flux measurements, 3A4
Neutron activation analysis
    (See Activation analysis)
Neutron cross sections
    (See Cross sections)
  measurement by mass spectrography and radiochemistry, 8A7
Neutron diffraction analysis
  acetylides, 2A74
  aluminum - chromium intermetallic compounds, 2A74
  chromium carbides, 2A74
  computer applications, 1A10
  fundamental studies, 8A35
  hafnium, 2A74
  high temperature phase studies, 2A54
  lithium carbides, 2A74
  lithium hydrogen carbides, 2A74
  magnesium carbides, 2A74
  magnetic materials, structural studies, 3A12
  magnetite, 2A74
  niobium carbides, 2A74
  peroxides, 2A74
  plutonium carbides, 2A74
  potassium hydrogen carbides, 2A74
  sodium carbides, 2A74
  tantalum carbides, 2A74
  terbium carbides, 2A74
  titanium carbides, 2A74
  uranium oxides, 2A71
Neutron diffractometers
  development, 2A74
Neutron fluxes
  spectra determination, 8A7
Neutrons
  diffraction studies of liquid structure, 8A24
  effects on deuteriated proteins, 2A52
  from fission fragments, 2A17
  irradiation facility using isotopes, 2A33
  prompt emission in fission, angular and energy distribution, 5A17
  thermal, fission yield measurements, 8A3
Nickel
  chronopotentiometry in molten fluorides, 8B2
  complexes with vic-dioximes, 1A3
  surface reactions with halogens, 6-1
  use in nitrofluor process, 3B4
Nickel-60
  decay studies, 2A4
Nickel intermetallic compounds ($TbNi_2$)
  neutron diffraction studies, 3A12
Nickel ions
  complexes with dibasic amino acids, infrared spectra, 7-39
  complexes with DL-leucine, infrared spectra, 7-39
  complexes with DL-norvaline, infrared spectra, 7-39
  complexes with DL-phenylalanine, infrared spectra, 7-39
  complexes with glycine, infrared spectra, 7-39
  half-wave potential and diffusion current in solutions, 7-33
Nickel oxide systems (Fe_2O_3-NiO)
  diffusion studies, 7-24
Nickel oxide systems (MgO-NiO)
  diffusion studies, 7-24
Nickel uranates
  crystal structure, x-ray diffraction studies, 2A71
  uranium-oxygen bond studies, 2A78
Niobium
  analysis by emission spectrography, 2A35
  corrosion and film studies in hydrogen fluoride solution, 8A18
  diffusion-controlled oxidation, 5B20
  fluorometric determination, 7-38
  removal from protactinium pentoxide, 2A54
  separations by hydrogen peroxide elution, 1A5
  separation from tantalum by halogenation, 1B9
  solvent extraction from acid solutions by amines, 8D3
Niobium-95
  isomer yields in fission, 2A14
Niobium-97
  yield from uranium-235 fission, 8A5
Niobium borides (NbB_2)
  enthalpy of formation, 2B10
Niobium carbides (NbC)
  neutron diffraction studies, 2A74
Niobium fluorides (NbF_5)
  enthalpy of formation, 2B10
Niobium iodides
  physical and chemical properties, 1A19
Niobium oxychloride
  chlorination, 1B9
Nitrate ions
  interaction with metal ions, spectral studies, 2A65
  reduction, isotope effects, 8A27
Nitrates
  radiolysis, effects of crystal structure, LET, and phase, 8A34
  irradiated single crystals, paramagnetic resonance spectroscopy, 8A10
  spectral studies, 2A87
Nitric acid
  anhydrous, catalytic properties, 5A61
  effects on ion exchange resins, 8D8
  reaction with hydrocarbons in solvent extraction processes, 8A31
  spectrophotometry over wide temperature ranges, 8A19
Nitric acid systems (HNO_3-TBP-H_2O)
  activity measurements, 8D2
Nitrites
  irradiated single crystals, paramagnetic resonance spectroscopy, 8A10
Nitrofluor process
  dissolution of fuel materials, 3B4
Nitrogen
  analytical determination in metals, 1A6
  determination by helium-3 activation analysis, 5A57
  determination in submilligram samples of organic compounds, 5A71
  diffusion studies, 8C11
  excitation by slow electron impact, 3A10
  free radicals, reaction rate studies, 5B17
  reactions with disulfur dichloride, 5B7
  reactions with hydrogen sulfide, 5B7
  reactions with sulfur vapor, 5B7
Nitrogen (liquid)
  oxygen radiation chemical reactions in, 8A34
Nitrogen-14
  nitrogen-15/nitrogen-14 shift, vibrational mode studies in various compounds, 1A8
Nitrogen-15

  analysis by mass spectrometry, 3A13
  enrichment in ammonia by ion exchange, 1A26
  nitrogen-15/nitrogen-14 shift, vibrational mode studies in various compounds, 1A8
Nitrogen-17
  formation cross sections, 3A1
  radioactive decay studies, 8A5
Nitrogen ions
  bombardment of californium for production of heavier elements, 5A5
Nitrogen oxide systems (HD-N_2O)
  energy transfer in ion-molecule interactions of, 3A10
Nitrogen oxides
  charge neutralization studies of ionized, 5B14
  electron reaction kinetics, 5B16
  solvent properties in nitrofluor process, 3B4
Nitrogen - sulfur compounds
    (See Sulfur - nitrogen compounds)
Nitrogen-sulfur ions
  reactions, 5B7
Nitrogen systems (HD-N_2)
  energy transfer in ion-molecule, interactions of, 3A10
Nitrophenol, carbonyl-
    (See Phenols, carbonyl nitro-)
Nitroso benzene
  oxidation with organic oxidizer, free radical formation, 1A14
Noble gases
    (See Rare gases)
Norvaline
  metal complexes, infrared spectra, 7-39
Nuclear chemistry
  computer calculations of the pairing Hamiltonian, 2A69
  data handling instruments, 8A6
  fission yield studies, 8A3
  fundamental studies, 3A1
  geochemical applications, 3A3
  hot-atom reactions, 3A6
  instrument development, 5A40
  neutron cross section determination, 8A7
Nuclear cross sections
    (See Cross sections)
Nuclear energy levels
  heavy elements, study by nuclear reaction techniques, 8A2
  spectroscopic investigations, 8A5
  structure in heavy elements, 8A2
Nuclear magnetic moments
    (See Magnetic moments)
Nuclear magnetic resonance
  acidic organophosphorus compounds, 2A87
  barrier studies with cyclic amides, 3A7
  deuteriated chlorophyll, 2A51
  dissociation of complexes in solution, studies by, 7-30
  electrolyte solution structural studies, 2A84
  of isotopic molecules, 8A26
  molecular structure studies, 5B25
  monochloro salicyl aldehydes, correlation with ptl values, 2A82
  organogermanium alkoxides, 7-36
  oxygen-17 measurements, water kinetic studies, 5B6
  of picryl-hydrazines, 2A73
  silicon hydrides, 5B8
  solvent extraction mechanism studies, 5A50
  solvent extraction studies, 4-2
  spectroscopy, isomer identification by, 8A29
  xenon fluorides in hydrogen fluoride and halogen fluoride solutions, 2A67
Nuclear masses
  measurements, instrument development, 2A27
Nuclear matrix elements
  beta decay, study by polarization measurements, 8A4
  study by beta decay, 2A25
Nuclear models
  assymetric rotor type, agreement of theory with experiment, 2A77
Nuclear models (liquid drop)
  fission barrier calculations, comparison with measurements, 5A21
  kinetic energy calculation comparison with measurements, 5A20
Nuclear models (shell)
  calculation of matrix elements of two-nucleon interactions, 5A14
  comparison of calculations with energy level schemes near double-closed shells, 5A7
  theoretical calculations, 5A15
Nuclear models (spherical)
    theoretical calculations, 5A15
Nuclear power
  economic study based on thorium reserves, 8D10
Nuclear reactions
    (See also Fission)
  ($\alpha,\alpha' f$), nuclear structure studies by, 2A5
  ($\alpha,2\alpha$), studies in several elements at high energy, 5A32
  (α,d), excitation of high-spin nuclear levels, 5A28
  ($\alpha,d\gamma$), angular correlation studies, 5A33
  (α, He^4), cross section vs. angle and energy, 5A32
  $Ar^{40}(t,p)Ar^{42}$, observation, 3B10
  B^{11}(He, T) C^{11}, recoil-fragment range-energy studies, 2A10
  B^{11}(p, n) C^{11}, recoil-fragment range-energy studies, 2A10
  C^{12}(n,2n) C^{11}, chemical effects, 3A5
  $C^{12}(\pi^-,\pi^- n)C^{11}$, excitation function and cross section, 5A31
  C^{12}(p, pn) C^{11}, differential recoil study, 2A11
  C^{12}(p, pn) C^{11}, recoil-fragment range-energy studies, 2A10
  $Cl^{37}(\nu,e^-)Ar^{37}$, use to measure neutrino flux from the sun, 3A4
  Co^{59}(p,α) Fe^{56}, 2A4
  Co^{59}(p,α) Fe^{56}, high-resolution studies, 2A2
  Co^{59}(p, p'), high-resolution studies, 2A2
  Co^{59}(p, α) Fe^{56}, cross section fluctuations, 2A6
  (d,α), mechanism clarification by study of (p,He^3) reaction, 5A27
  energy-level studies on heavy elements, 8A2
  evaporation spectra studies, 2A4
  (γ, f) thresholds for heavy nuclei, 2A1
  (γ,n), chemical effects, 1A22
  (γ, n) yields, 2A1
  (γ, p) yields, 2A1
  Au^{197}(p, spallation) Tb^{149}, excitation functions, 3A1
  He^3(p,d) 2p, use to study proton-proton interactions, 5A25
  He^3(d,t) 2p, use to study proton-proton interactions, 5A25
  high energy, mechanism of, 5A24
  induced by high-energy particles, 2A16
  Fe^{56}(α, α'), 2A4
  Fe^{56}(p,p'), high-resolution studies, 2A2
  $Fe^{58}(t,n)Co^{58}$, observation, 3B10
  $Pb^{208}(He^4,He^3)$ Pb^{209}, theory, 2A1
  $Mg^{25}(t,\alpha)Na^{24}$, excitation function, 3B10
  $Mg^{26}(t,p)Mg^{28}$, excitation function, 3B10
  Mn^{55}(p,α) Cr^{52}, high-resolution studies, 2A2
  Mn^{55}(p,p'), high-resolution studies, 2A2
  (n,γ), chemical effects, 1A22
  $Ni^{58}(t,n)Cu^{59}$, cross section, 3B10

  $N^{14}(p,\alpha)$ C^{11}, chemical effects, 3A6
  of pions, 5A31
  $Pu^{238}(\alpha,2n)$ Cm^{238}, 2A1
  (p,He^3), study to clarify mechanism of (d,α) reaction, 5A27
  $(p, p\pi^+)$, fundamental studies, 2A13
  (p,t), energy level studies of various nuclei, 5A27
  proton-induced, theoretical studies, 2A70
  of protons, helium-3, and helium-4, 5A29
  recoil atoms, chemical effects, 5A58
  recoil fragments, range-energy studies for heavy, 2A10
  studies with magnetic spectrograph, 2A2
  spectroscopic studies, 3A2
  $S^{34}(n,r)$ S^{35}, chemical reactions of recoil atoms, 5A58
  theoretical studies, 5A37
  theories, kinetic energy calculation comparison with measurements, 5A20
  $U^{234}(d, pf)$, use to study near-threshold fission of uranium-235, 2A15
  $U^{235}(\alpha,3n)$ Pu^{236}, 2A1
  $U^{235}(d, xn)$ Np^{237-x}, neptunium isomer production by, 2A22
  $U^{238}(\alpha,\alpha'f)$, cross section studies, 2A5
  $U^{238}(d, xn)$ Np^{240-x}, neptunium isomer production by, 2A22
Nuclear spectra
    (See Spectra (nuclear))
Nuclear spin
  cerium-143, 5A13
  gadolinium-153, 5A13
  of fission fragments, 2A14
  promethium-148, 5A13
Nuclear structure
  deformed heavy elements, spectroscopic studies, 5A10
  deformed nuclei, theoretical calculations, 5A15
  electron spectrometry studies, 5A4
  internal conversion coefficient in studies of, 5A3
  nuclei near lead-208, 5A8
  nuclei in transition region between sphericity and strong deformation, 5A9
  prompt gamma ray emission studies, 5A17
  study by spectroscopy, 3A2
  theoretical calculations, 5A15
  theoretical studies, 5A37
Nuclei
  coulomb excitation studies using heavy ions, 5A36
  decay schemes of, near double-closed shells, 5A7
  deformation region, studies of neutron-deficient praseodymium isotopes, 5A6
  deformed, energy level studies, 8A5
  energy levels, high-precision electron spectrometric studies, 5A4
  energy levels in region of fission barriers, 5A16
  gamma rays, angular correlation, 5A47
  heavy, energy-level structures, 8A2
  interaction mechanism with charged particles, 5A24
  medium-weight, energy level studies, 8A5
  orientation for angular distribution determination of emitted charged particles, 5A1
  orientation by external field polarization, 5A2
  polarization, induced magnetic field studies, 5A47
  study for heavy elements, 2A7
Nucleic acids
  reactions, low temperature studies, 3A11
  role in learning process of planarians, 3A11
Olefins
    (See Aliphatic compounds)
Optical pumping
    (See also Lasers)
  mercury, 5A72
  neon, 5A72
Optical rotatory dispersion
  camphor, 2A57
  chemical reactions and equilibria, 2A57
  quartz, 2A57
Organic chemistry
  analytical services at BNL, 3A13
  crystallography studies, 3A12
  theoretical, structure studies, 3A9
Organic compounds
    (See also Aliphatic compounds, Aromatic compounds, Hydrocarbons, and specific compounds by name)
  adsorption, effect on corrosion of metals, 8A17
  aromatic, radiation chemistry, 2A48
  determination of radiative lifetime in excited state, 5B3
  luminescence decay-time studies, 7-13
  luminescence, energy transfer mechanisms, 7-8
  metastable electronic states, observations, 5A45
  photoionization studies, 6-4
  radiation chemistry, role of ions, 5A59
  radicals, electron-spin-resonance studies, 7-12
  radiolysis, 7X2
  recoil chemistry of carbon-11, 1A29
  simultaneous determination of elements in submilligram samples, 5A71
  structure of high molecular weight, 2A27
Organic glasses
  gamma-irradiation effects, 7-16
Organic solvents
  actinide complexes in, 4-3
  interaction with inorganic compounds, 4-2
  isotope exchange reactions with amalgams, 8A27
Organogermanium alkoxides
  disproportionation, 7-36
  preparation, 7-36
Organometallic compounds
  radiation and photochemistry in benzene, 7-3
Organophosphorus compounds
  acid strength of substituted forms, 2A88
  acidic, proton magnetic resonance studies, 2A87
  acidic, spectral studies, 2A87
  extractant effectiveness of substituted forms, 2A88
  interaction with hydrogen bond donors and acceptors, 2A86
  molecular complexity in various diluents, 2A89
  rare earth extraction by, 2A89
  solvent extraction studies, 4-2
  use as solvent extractants, 1A2
Osmium
  nuclear studies in the vibrational region, 5A35
Oscillating jets
  liquid - liquid interface studies by, 5A64
Osmium fluorides (OsF_6)
  quantum mechanical studies of electronic-nuclear interactions, 2A75
Oxidation
  anodic, of liquid phosphorus in aqueous media, 5B30
  californium, 2A60
  diffusion-controlled, in refractory metals, 5B20
  einsteinium, 2A60
  electron exchange processes, 3A8
  ion exchange resins, 8D8
  iron ions by cobalt ions in presence of chloride ions, 3A8
  isotopic studies of mechanisms, 8A28
  measurement in micron-size fissure electrodes, 5B28
  in organic solutions, free radical formation, 1A14
  rare earths in fused nitrate solutions, 2A62
Oxide ions

  - chronopotentiometry in molten fluorides, 8B2
- Oxides
  - high temperature chemical and physical studies, 2A54
  - oxygen determination in, 2A36
  - refractories, surface chemistry in aqueous media, 8C3
  - solubility in molten salts, 8C9
- Oximes
  - reduction by mixed hydrides, stereochemistry, 7-28
- Oxygen
  - adsorption on metal oxides, stresses produced by, 7-23
  - analytical determination in metals, 1A6
  - determination by activation analysis, 1A28
  - determination, development of methods for, 2A36
  - determination by helium-3 activation analysis, 5A57
  - diffusion studies, 8C11
  - effect on pyrolysis of hydrocarbons, 5A75
  - molecular ions, structure, 7-15
  - reaction with free radicals, electron paramagnetic resonance studies, 5B17
  - reduction kinetics, 8C4
  - removal from liquid metals by hydrogen reduction, 5A66
- Oxygen-16
  - (α,d) reaction, excitation of spin-5 level in fluorine-18 product, 5A28
  - (p,t) reaction, nuclear energy level studies, 5A27
- Oxygen-17
  - nuclear energy level studies, 8A5
  - nuclear magnetic resonance, water kinetic studies, 5B6
- Oxygen-18
  - analysis by mass spectrometry, 3A13
- Oxygen-16 ions
  - bombardment of holmium to produce rhenium-181, 5A21
  - bombardment of various elements, fission excitation function measurements, 5A21
  - irradiation of rare earths for platinum isotope production, 5A11
- Oxygen free radicals
  - reaction rate studies by electron paramagnetic resonance, 5B17
- Oxygen systems (HD-O_2)
  - energy transfer in ion-molecule interactions of, 3A10
- Oxygen systems (O-U)
  - phase studies at high temperatures and pressures, 2A56
- Oxyhalides
  - physico-chemical characterization by mass spectrometry, 1A17
- Ozone
  - formation by radiation chemical reactions of oxygen in liquified gases, 8A34
- Paintings
  - analytical studies at BNL, 3A13
- Palladium-111
  - isomer yields in fission, 2A14
- Palladium ions
  - complexes with DL-leucine, infrared spectra, 7-39
  - complexes with DL-norvaline, infrared spectra, 7-39
  - complexes with DL-phenylalanine, infrared spectra, 7-39
  - complexes with glycine, infrared spectra, 7-39
- Paramagnetism
  - in solids, fundamental studies, 1A12
- Particle accelerators
  - (See also Cyclotrons and Heavy Ion Linear Accelerators)
  - development for nuclear reaction studies, 8A2
  - high energy charged particles for nuclear reaction studies, 5A24
- Pentane, 3-methyl-
  - luminescence spectra, 7-11
- Peptides
  - radiolysis, 5A77
- Perchlorate ion
  - interaction with metal ions, spectral studies, 2A65
- Perchlorates
  - hydrolytic reactions in aqueous solution, 8A12
- Perchloric acid
  - anhydrous, catalytic properties, 5A61
  - spectrophotometry over wide temperature ranges, 8A19
- Perfluoronaphthalene
  - (See Naphthalene, perfluoro-)
- Perfluorobicyclohexyl
  - (See Bicyclohexyl, perfluoro-)
- Perfluorobiphenyl
  - (See Biphenyl, perfluoro-)
- Perfluorodecalin
  - (See Decalin, perfluoro-)
- Peroxides
  - neutron diffraction studies, 2A74
- Peroxo-dicobalt complexes
  - electron paramagnetic resonance studies, 2A73
- Perturbation theory
  - electronic-nuclear interaction studies, 2A75
- pH
  - correlation with nuclear magnetic resonance of monochloro salicylaldehydes, 2A82
- Phase studies
  - binary alloy systems in regenerative cells, 2B7
  - effusion method for intermetallics, 2B4
  - in fluoride systems, 8C10
  - fused salts, 8C9
  - fused salts in regenerative cells, 2B7
  - high temperature studies, 2A54
  - intermetallics between lanthanide rare earths and group IIB elements, 2B4
  - lithium hydride systems in regenerative cells, 2B6
  - metals at high pressure, 5B11
  - phase effects on radiolysis, 8A34
  - rare earth sesquioxides, 2A56
  - transition metals, 5B1
  - uranium-oxygen system at high temperatures and pressures, 2A56
- Phenanthroline
  - interaction with hydrogen ions in aqueous solution, 1A1
- Phenols, carbonyl-
  - anions of, interaction with rare gas cations, 2A81
- Phenols, carbonyl nitro-
  - inter- and intra-molecular hydrogen bonding, 2A82
- Phenoxy group
  - effects on extraction effectiveness of organophosphorus compounds, 2A88
- Phenyl group
  - effects on extraction effectiveness of organophosphorus compounds, 2A88
- Phenylalanine
  - (See Alanine, phenyl-)
- Phenylazotriphenyl methane
  - reaction with benzene-di, isotope effects, 7-27
- 3-Phenyl 2-butanone
  - (See 2-Butanone, 3-phenyl-)
- Phenylcinnamic acid
  - (See Cinnamic acid, phenyl-)
- Phosphates
  - ion exchange and adsorption properties, 8A23
  - organic, oxygen analysis in, 2A36
- Phosphides
  - high temperature chemical and physical studies, 2A54
- Phosphine
  - (See also Phosphorus hydrides (PH_3))
- Phosphorescence
  - (See also Luminescence)
  - benzene, quantum yield for, 2A49

- Phosphoric acid
  - anhydrous, catalytic properties, 5A61
- Phosphoric acid, di 2-ethyl hexyl-
  - molecular complexity in various diluents, 2A89
- Phosphoric acid, di para (1,1,3,3 tetramethyl butyl phenyl-)
  - molecular complexity in various diluents, 2A89
- Phosphorus
  - analysis in meteorites, 2A30
  - organic compounds of, use as solvent extractants, 1A2
- Phosphorus (liquid)
  - anodic oxidation in aqueous media, 5B30
- Phosphorus-31
  - $(p, p\pi^{+})$ reaction, 2A13
- Phosphorus-32
  - beta particles, polarization measurements, 8A4
  - tracer use in planarian learning process studies, 3A11
- Phosphorus compounds
  - (See Organophosphorus compounds)
- Phosphorus hydrides (PH_3)
  - effects of electric discharge on, 5B8
- Phosphorus - sulfur bonds
  - infrared spectra, 7-31
- Photochemistry
  - chelates of polyfunctional ligands, 7-35
  - energy paths in, 2A49
  - free radical production at cryogenic temperatures, 7-25
  - ionization in low-pressure gases, 6-4
  - ionization studies, 5B15
  - laser applications, 7-14
  - of organometallics in benzene, 7-3
  - reaction initiation studies, 8A34
  - ultraviolet source, design of accurately reproducible, 7-9
  - using ultraviolet radiation, 6-3
  - vacuum ultraviolet studies, 7-2
  - xenon fluoride formation studies, 2A47
- Photolysis
  - of xylene isomers, 2A48
  - of xenon difluoride, 2A47
- Photons
  - correlations in helium neon laser beam, 5A73
- Photosynthesis
  - deuterium effects, 2A51
  - studies by chromatography, 2A32
- Phthalic acid
  - absorption spectra of hydrated electrons in aqueous solutions of, 2A43
- Physical chemistry
  - acidic organophosphorus compounds, 2A87
  - biochemical processes, 3A11
  - crystallography studies, 3A12
  - gas phase reactions, 3A10
  - inorganic salts, 2A87
  - interaction between organophosphorus and hydrogen bond donors and acceptors, 2A85
  - organic system structures and reactivities, 3A9
  - oxidation-reduction studies, 3A8
  - synthetic organic ion exchangers, 8A14
- Piaselenols
  - reduction studies, 3B8
- Picric acid
  - absorption spectra of hydrated electrons in aqueous solutions of, 2A43
- Picryl-hydrazines
  - nuclear magnetic resonance studies, 2A73
- Pigments
  - chloroplast, reactivity of deuteriated, 2A51
- Pions
  - nuclear interactions, 5A31
  - pion-pion interaction cross sections, 2A13
- Planaria
  - learning process, tracer studies, 3A11
- Plants
  - growth in heavy water, 2A50
- Plastics
  - radiolysis, LET effects, 8A34
- Platinum
  - catalytic activity, effect of stored energy, 7-21
  - ethane molecular beams, interaction with, 8A21
  - filament use in surface ionization of alkali metal compounds, 2A53
  - nuclear studies in the vibrational region, 5A35
- Platinum complexes
  - substitution reaction rates, 1A24
- Platinum fluorides (PtF_6)
  - quantum mechanical studies of electronic-nuclear interactions, 2A75
- Platinum ions
  - complexes with DL-leucine, infrared spectra, 7-39
  - complexes with DL-norvaline, infrared spectra, 7-39
  - complexes with DL-phenylalanine, infrared spectra, 7-39
  - complexes with glycine, infrared spectra, 7-39
- Platinum isotopes
  - decay schemes, 5A11
  - production by irradiation of rare earths with heavy ions, 5A11
- Platinum metals
  - (See also specific platinium metals, e.g., Osmium)
  - chemistry of complexes, 1A24
- Plutonates
  - preparation in fused salt solutions, 2A62
- Plutonium
  - emission spectroscopy, 2A72
  - ions, solid-state spectra studies, 5A55
  - irradiation with helium ions and deuterons, 2A1
  - spectrophotometry of solutions at high temperatures and pressures, 8D15
- Plutonium-236
  - alpha particle irradiations, 2A1
- Plutonium-238
  - neutron fission cross sections, 2A8
- Plutonium-239
  - coulomb excitation studies using heavy ions, 5A36
  - fission, tellurium isomer yields, 2A14
- Plutonium-240
  - photofission, 2A1
- Plutonium-241
  - neutron fission cross sections, 2A8
- Plutonium-242
  - neutron cross sections, 2A8
  - photofission, 2A1
- Plutonium-243
  - neutron cross sections, 2A8
- Plutonium-244
  - nuclear properties, 2A7
- Plutonium alloys
  - analysis by emission spectrography, 2A55
- Plutonium alloys (Cd-Pu)(liquid)
  - thermodynamic properties, 2B3
- Plutonium alloys (Pu-Zn)(liquid)
  - thermodynamic properties, 2B3
- Plutonium carbides (Pu_2C_3)
  - neutron diffraction studies, 2A74
- Plutonium compounds
  - analysis by emission spectrography, 2A55
- Plutonium chlorides ($PuCl_3$)
  - thermal expansion and crystal structure, 5A42
- Plutonium fluorides (PuF_5)
  - volatilization studies, 8D16
- Plutonium oxides

  preparation in fused salt solutions, 2A62
Plutonium oxides (PuO_2)
  high temperature properties, 2A60
Polarization
  beta particle studies, 8A4
  of high-energy proton beams, 5A26
  nuclear, use of external magnetic fields, 5A2
Polarography
  chelates of polyfunctional ligands, 7-35
  instrument development, 8B3
  of ions and complex compounds in dioxane-water media, 7-33
  metal ions in sulfuric acid solutions, 7-37
  sine wave A.C., chemical analysis by, 1A1
Polonium-205
  nuclear structure, gamma ray spectra studies, 5A8
Polyelectrolytes
  ion exchange, physical chemical studies, 8A14
Polymerization
  of propionamide and acrylamide, spectroscopic studies, 3B7
  protactinium in sulfuric acid solutions, 8D9
Polymers
    (See also specific polymers by name e.g., Butadiene polymers, Protactinium polymers, etc.)
  oxygen bridging studies by oxygen-17 nuclear magnetic resonance, 5B6
  radiation chemistry, 8C1
  radioactive, cross-linked cation exchanger studies, 8A14
Potassium-40
  decay constants, 2A21
Potassium-46
  search for, 3B10
Potassium-47
  search for, 3B10
Potassium-48
  search for, 3B10
Potassium alloys (K-Na)(liquid)
  thermodynamic properties, 2B2
Potassium - argon dating
    (See Age determination)
Potassium chloride
  color centers in crystals, spectroscopic studies, 7-22
Potassium chloride systems ($CdCl_2$-KCl)
  calorimetric studies of complexes in fused, 6-10
Potassium chloride systems (KCl-LiCl)(liquid)
  solvent use in rare earth absorption spectra studies, 2A61
Potassium chloride systems (KCl-LiCl-UCl_4)(liquid)
  chlorination rate of uranium tetrachloride in, 5B18
Potassium chloride systems (KCl-NaCl)(liquid)
  metal freezing by, in liquid metal extraction studies, 5B19
Potassium hydrogen carbides (KHC_2)
  neutron diffraction studies, 2A74
Potassium hydrogen chloromaleate
  neutron diffraction studies of structure, 8A35
Potassium lanthanum nitrates
  crystal growth in fused salt solutions, 2A62
Potassium nitrate systems (KNO_3-$LiNO_3$)(liquid)
  potentiometric studies, 3B9
  rare earth oxide preparation in, 2A62
  solvent use in rare earth absorption spectra studies, 2A61
  solvent use in rare earth excited state studies, 2A62
Potassium pertechnetate
  heat capacity, low-temperature measurements, 8A11
Potassium - potassium bonds
  energy, 5B15
Potassium praseodymium nitrates ($K_3Pr_2(NO_3)_9$)
  crystal structure, x-ray diffraction studies, 2A71
Potassium rhenium fluoride
  low-temperature heat capacity, 8A11
Potassium rhenium iodide
  low-temperature heat capacity, 8A11
Potassium sulfate
  electrical conductance in water at high temperature and high pressure, 8C6
  solubility in water at high temperature, 8C7
Potassium technetium chloride
  heat capacity, low-temperature measurements, 8A11
Potassium uranates
  crystal structure, x-ray diffraction studies, 2A71
Potentiometry
    (See also Chronopotentiometers)
  fused-salt studies, 3B9
  study of aqueous salt solutions, 8C5
Praseodymium-130
  gamma ray spectra of decay products of, nuclear deformation region studies, 5A6
Praseodymium-132
  gamma ray spectra of decay products of, nuclear deformation region studies, 5A6
Praseodymium-134
  gamma ray spectra of decay products of, nuclear deformation region studies, 5A6
Praseodymium-135
  decay scheme, spectrographic observations, 8A8
Praseodymium-142
  magnetic moment measurement, 5A13
Praseodymium alloys (Cd-Pr)(liquid)
  phase studies, 2B4
  thermodynamic properties, 2B3
Praseodymium alloys (Pr-Zn)(liquid)
  phase studies, 2B4
Praseodymium halides
  electronic conductivity of metal solutions, 1A20
Praseodymium ions
  configuration interactions, 5A43
Praseodymium potassium nitrates ($K_3Pr_2(NO_3)_9$)
    (See Potassium praseodymium nitrates ($K_3Pr_2(NO_3)_9$))
Pressure
  effects on coordination number of metal ions in fused salt solutions, 2A63
  effects on phase relations in metals, 5B11
  effects on thermal conductivity of insulators, 5B12
  effects on thermodynamic properties of metals, 5B10
  ultra-high, Mossbauer effect under, 5B13
  ultra high, phase studies, 2A56
Promethium
  search for naturally occurring, 2A31
Promethium-148
  hyperfine structure studies, 5A13
  nuclear spin determination, 5A13
Promethium fluorides (PmF_3)
  crystallography, 5A42
1-Propanone, 2-diphenyl-
  reduction by lithium aluminum hydride, stereochemistry, 7-28
Propionamide
  solid-state polymerization, spectroscopic studies, 3B7
Protactinium
  emission spectroscopy, 2A72
  hydrofluoric acid solutions, Raman spectra, 8A1
  preparation from protactinium tetra-fluoride, 2A64
  spectrophotometry of solutions at high temperatures and pressures, 8D15
Protactinium-227
  decay scheme, 5A9
Protactinium-229

  decay scheme, 5A9
Protactinium-231
  chemical properties, 2A64
Protactinium complexes
  spectral studies, 8D9
Protactinium fluorides
  preparation, 2A64
  synthesis of complex, 8A1
Protactinium fluorides (PaF_4)
  reduction to metal, 2A64
Protactinium oxides (Pa_2O_5)
  purification, 2A64
Protactinium oxyfluorides
  preparation, 2A64
Protactinium polymers
  preparation in sulfuric acid solutions, 8D9
Proteins
  deuteriated, properties of, 2A52
Proton magnetic resonance
  of Lewis acids and Lewis bases, 7-34
Protons
  beams, scattering and polarization at high energy, 5A26
  bombardment of targets in studies of nuclear reactions, 5A24
  high-energy, collisions with hydrocarbon molecules and noble gas atoms, 2A38
  high-energy, fission reactions by, 2A9
  high-energy reactions, 2A16
  induction of two-nucleon pick up reactions, 5A27
  interaction with protons, 5A25
  nuclear reaction induction, theoretical studies, 2A70
  nuclear reactions, mechanisms of low-energy, 5A29
  scattering by protons, correlation coefficients, 5A30
  semiconductor detection instruments, 8A2
Protozoa
  growth in heavy water, 2A50
Pulse amplifiers
  design and development, 5A39
Pulse columns
  evaluation of operating characteristics, 8D4
Pulse electrolysis
    (See Electrolysis)
Pulse-height analyzers
  design for coincidence spectroscopy, 8A6
Pulse radiolysis
    (See Radiolysis)
Purification
  protactinium pentoxide, 2A64
  xenon hexafluoride, 2A66
Purpurin
  chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
  reduced, chelates with di-, tri-, and tetra- valent metal ions, properties of, 7-35
Pyridines
  chelates, formation and dissociation constants, 7-33
Pyridines, methyl-
  radiation chemical studies, 2A48
Pyrolysis
  of hydrocarbons, effect of oxygen, 5A75
  ion exchange resins, 8D8
  rare earths in fused nitrate solutions, 2A62
Pyrolytic graphite
  deposition from hydrocarbon-hydrogen system, 3B2
Quantum mechanics
  of energy transfer and molecular interactions, 7-20
  fission barrier studies, 5A16
  hexafluoride molecule high energy electronic state studies, 2A75
  isotope effects studies, 3A7
  liquid helium-3 studies, 2A79
  of unstable molecules, 6-7
Quantum yield
  fluorescence of benzene, 2A49
  xenon difluoride formation, 2A47
Quartz
  electron paramagnetic resonance studies, 2A73
  optical rotatory dispersion studies, 2A57
8-Quinolinato tin
  Mossbauer effect in, 7-29
Racemic isomers
  identification by nuclear magnetic resonance spectroscopy, 8A29
Radiation
  excitation of electronic states in matter, 7-17
Radiation biology
  transient species studies in irradiated oxygenated water, 2A45
Radiation chemistry
    (See also G-values and Radiolysis)
  absorption spectra of transient species in aqueous solutions, 2A43
  aliphatic alcohols, solvated electron formation, 2A41
  of amino acids and peptides, 5A77
  aromatic compounds, 2A48
  chelates of polyfunctional ligands, 7-35
  cis-trans isomerization of stilbene in benzene, 7-4
  Cu^{65}(p,pn), recoil studies, 3A1
  crossed-beam studies of reactions of accelerated atoms with molecules, 2A39
  electron-spin-resonance studies, 7-12
  energy transfer studies in solid, liquid, and gas systems, 8A34
  fission-fragment induced reactions, 5B23
  fluorine release from inorganic fluorides, 8C2
  of fluorocarbons, 3B3
  fundamental studies, 3A1
  fundamental studies, 3A5
  of Group IVB metal alkyls in benzene and cyclohexane, 7-7
  hot-atom reactions, 3A6
  interactions of electrons and positive ions with molecules in gaseous phase, 3A10
  ionic and hot-radical reactions, 6-2
  laser applications, 7-14
  mass spectrometer applications, 8A22
  mechanisms, 8A33
  molecular ions in crystals, 8A32
  of noble-gas compounds, 3B3
  of organic glassy systems, 7-16
  of organic materials, 3B7
  organic solid state studies, 2A40
  of organic systems, 7X2
  of organic systems, role of ions, 5A59
  of organometallics in benzene, 7-3
  oxygenated water, 2A45
  polymers, studies on, 8C1
  pulsed radiolysis studies, 2A42
  pulsed radiolysis studies, 2A44
  reactions induced by fission fragments, 3B6
  track reactions, 7-19
Radiation detectors
  development of semiconductor, 5A38
Radiation dose
    (See Dose (radiation))
Radiation effects
    (See also Radiolysis)
  on alkali metal halates, 8A32
  on alkaline earth halates, 8A32
  on analytical chemistry, 8B4

  on aqueous corrosion of zirconium alloys, 8C4
  on coalescence, 8D5
  on fluorocarbons, 3B3
  on ion exchangers, 8D8
  on polymerization of organic materials, 3B7
  on solvents, 8D2
Radiation targets
  bombardment with charged particles in studies of nuclear reactions, 5A24
Radicals
    (See also Free radicals)
  formation by irradiation of organic materials, ESR studies, 7-12
  formation in organic glassy systems by gamma irradiation, 7-16
  reactions in charged-particle tracks, 7-19
Radioactive decay
  coincidence spectroscopy, 8A6
  determination for radioisotopes, 2A22
  determination for radioisotopes, 2A23
  Einsteinium-254m, 5A10
  fermium-255, 5A10
  nuclei near double-closed shells, 5A7
  platinum isotopes, 5A11
  protactinium-227, 5A9
  protactinium-229, 5A9
  of radioisotopes of geochemical interest, 2A21
  uranium-235m, calorimetric determination of energy, 5A12
Radioactive materials
  remote chemical analysis, instrument development, 8B3
Radiochemistry
  fission yield studies, 8A3
  ion exchange processes, 8D8
  neutron cross section measurements by, 8A7
  nuclear reaction product studies, 5A24
  rare gas measurement after desorption from charcoal, 2B1
Radiography
    (See Autoradiography)
Radioisotopes
    (See specific radioisotopes)
Radiolysis
  of ammonia, effect of density, 7-5
  of ethane, effects of density, 7-6
  gas phase, effects of ions and excited states, 8A34
  ion exchange resins, 8D8
  mechanisms, 8A32
  mechanisms, 8A33
  pulse-type, absorption spectra of transient species in aqueous solutions, 2A43
  pulse-type, aqueous ferrocyanide solution studies, 2A44
  pulse-type, aqueous tetranitromethane solution studies, 2A44
  pulse-type, effects on transient conductivity of water, 2A46
  pulse-type, hydrated electron reaction rate studies, 2A42
  pulse-type, hydroxyl radical reaction rate studies, 2A42
  pulse-type, liquid ammonia studies, 2A44
  pulse-type, oxygenated water studies, 2A45
  pulse-type, solvated electron formation, 2A41
  pulsed-type, studies in hydrogen-saturated alkaline aqueous solutions, 2A44
  pulse-type, xenon-fluorine mixture studies, 2A47
  of xylene isomers, 2A48
Radium
  emission spectroscopy, 2A72
  removed by ion exchange in uranium ore processing, 8D12
Radium-226
  fission by protons, mass distribution studies, 2A18
  fission studies with high-energy helium ions, 2A19
Radon
  chemical properties, 2A58
  thermodynamic properties, determination from solubility in liquid alkali metals, 2B1
Radon compounds
  preparation for mass spectrometry, 2A68
  production and identification, 2A58
Radon fluorides
  identification, 2A58
  synthesis, 2A66
Raman spectra
    (See Spectra (Raman))
Rare earth chlorides
  aqueous solutions, thermodynamics, 1A13
Rare earths
  magnetic properties, 1A12
  molten salt solutions, 8A25
  separations by ion exchange, 1A5
  separation by ion exchange, 1A25
  separation by solvent extraction, 1B8
  solvent extraction from acid solutions with amines, 8D3
  solvent extraction with nitrobenzene-iodine solution, 3B5
  tantalum determination by activation analysis, 1A28
Rare earths (actinides)
    (See also specific actinide rare earths e.g., Thorium, Protactinium, etc.)
  absorption spectra, 2A61
  analytical chemistry, radiation effects, 8B4
  chemical properties, 2A60
  complexes, chemical bonding studies, 4-3
  compounds, crystal structure studies, 5A42
  compounds of, low temperature calorimetric studies, 2A80
  compounds, synthesis and structure, 8A1
  coordination chemistry in molten salts, 4-1
  deuterides of, low temperature calorimetric studies, 2A80
  electronic configuration, Mossbauer effect studies, 5A48
  electronic spectra in molten salts, 4-1
  extraction by organophosphorus compounds, 2A89
  fission properties, 2A20
  fluorescence spectra, 2A61
  ions, paramagnetic resonance studies, 5A52
  isomeric states, production, 2A1
  neutron cross sections, 2A8
  preparation of compounds, 2A60
  separation from lanthanides by solvent extraction, 8A31
  separation techniques, 2A60
  solid-state spectra studies, 5A55
  solvent extraction studies, 3B8
  solvent extraction studies, 4-2
  spectra of free atoms, 5A56
  spectra, theoretical studies, 2A76
  spontaneous fission studies, 2A1
  sulfides of, magnetic susceptibility, 2A83
  thermal decomposition to oxides in fused nitrate solutions, 2A62
  thermochemistry studies, 5A53
  transplutonic, separations chemistry, 2A90
Rare earths (actinides)(liquid)
  thermodynamic properties of binary solutions with other metals, 2B3
Rare earths (lanthanides)
    (See also specific lanthanide rare earths e.g., Cerium, Praseodymium, etc.)
  absorption spectra, 2A61
  absorption spectra in oxy-acetylene flames containing ethanol solutions of perchlorates, 1A8
  complexes, stability constants, 1A27

compounds, crystal structure, 5A42
covalency, 2A65
electronic configuration, Mossbauer effect studies, 5A48
extraction by organophosphorus compounds, 2A89
fluorescence spectra, 2A61
irradiation with heavy ions for platinum isotope production, 5A11
separation from actinides by solvent extraction, 8A31
sesquioxides of, phase studies, 2A56
spectra, theoretical studies, 2A76
thermochemistry studies, 5A53

Rare earths (lanthanides)(liquid)
phase studies of binary solutions with group IIB metals, 2B4
thermodynamic properties of binary solutions with cadmium, 2B3

Rare gases
atom collisions with high-energy protons, 2A38
cations of, interactions with other ions, 2A81
compounds with fluorine, radiation chemistry, 3B5
effects on synthesis of water from hydrogen and oxygen, 8A54
fluorides, chemical properties, 2A66
heat capacity of solid, 5B24
ionization, experimental threshold laws by mass spectrometry, 2A85
mass spectrometry of compounds of, 2A68
solubility in liquid alkali metals, 2B1
systems, electronic spectra of atoms and molecules in, 5B4
thermodynamic properties, 2B1

Reactions
(See also Nuclear reactions)
gas molecules in excited state, 5A10
gaseous free radicals, electron paramagnetic resonance studies, 5B17
initiation by fission fragments, 5B6
intermediate species, identification in gases, 5B26
isotope effects, 5A7
isotope effects, 8A27
isotope effects, 8A28
kinetics of inorganic, 1A15
mass spectrometer applications, 8A22
of nuclear recoil particles, 1A29
oxidation-reduction kinetics studies, 5A8
rate processes at metal-gas interfaces, 6-1
reaction equipment, 5A65
with recoil atoms from nuclear reactions, 5A58

Reactors
neutron reaction rates, estimation, 8A7
neutron source in diffraction studies of magnetic materials, 5A12

Recoil fragments
from nuclear reactions, chemical effects, 5A58
range-energy studies for nuclear reactions, 2A10
studies on carbon-11, 2A11

Redistribution reactions
for unsymmetrical primary trialylboranes, 7-32

Refractory metals
(See also specific refractory metals, e.g., Tungsten)
diffusion-controlled oxidation, 5B20
electronic configuration, Mossbauer effect studies, 5A48
iron removal process design, 5B2
passive oxide layers, electrochemical studies, 8A18
plutonium contaminated, oxygen determination in, 2A36

Refractory materials
dissolution, radiation effects on, 8B4
surface chemistry in aqueous media, 8C3

Regenerative cells
bimetallic types, 2B7
bimetallic types, 2B8
electrode kinetics studies, 2B9
lithium hydride system studies, 2B6
solubility of intermetallic compounds in fused salts, 2B8
thermodynamic property studies of binary alloys, 2B7

Resins
ion exchange, chemical and radiation stability, 8D8

Resonance lamps
development for photochemical studies, 6-5

Reviews
thermodynamic data for electrolyte solutions, 6-11

Rhenium
filament use in surface ionization of alkali metal compounds, 2A55
work-function measurement by surface ionization, 5A51

Rhenium-181
formation by bombardment of various elements with heavy ions, 5A21

Rhenium-185
coulomb excitation studies using heavy ions, 5A36

Rhenium-187
coulomb excitation studies using heavy ions, 5A36

Rhenium compounds
thermodynamic properties, measurement, 8A11

Rhenium fluorides (ReF$_6$)
magnetic susceptibility, 2A83
quantum mechanical studies of electronic-nuclear interactions, 2A75

Rhenium isotopes
hyperfine structure studies, 5A13
magnetic moment measurement, 5A13

Rhodium fluorides (RhF$_6$)
quantum mechanical studies of electronic-nuclear interactions, 2A75

Ribonuclease
role in learning process of planarians, 5A11

Rocks
thorium recovery, geologic aspects, 8D11
thorium reserves and process costs, 8D10

Rubidium-87
decay constants, 2A21

Rubidium - rubidium bonds
energy, 5B15

Rubidium uranates
crystal structure, x-ray diffraction studies, 2A71

Ruthenium
solvent extraction from acid solutions by amines, 8D3

Ruthenium fluorides (RuF$_6$)
quantum mechanical studies of electronic-nuclear interactions, 2A75

Rutherford scattering
light-element analysis by, 2A28

Salicylaldehydes, chloro-
correlation of pH values with nuclear magnetic resonance, 2A82

Salts
(See also Fused salts)
aqueous chemistry at high temperature, 8C5
electrical conductance in water at high temperature and high pressure, 8C6
inorganic, physical chemical studies, 2A87
solubility in water at high temperature, 8C7

Samarium
valence state produced by radiolysis of aqueous solutions, 8A33

Samarium-151
half-life determination, 2A21

Sapphire
calorimetric studies of synthetic types, 2B13

Scandium
  reaction with its molten chloride and iodide, 1A20
Scandium-42
  excitation in $Ca^{40}(\alpha,d)$ Sc^{42} reaction, 5A28
Scandium-51
  search for, 3B10
Scandium benzilate complexes
  stability constants, 1A27
Scandium glycolate complexes
  stability constants, 1A27
Scandium glyoxylate complexes
  stability constants, 1A27
Scandium hydroxyisobutyrate complexes
  stability constants, 1A27
Scandium isobutyrate complexes
  stability constants, 1A27
Scandium lactate complexes
  stability constants, 1A27
Scandium methoxyacetate complexes
  stability constants, 1A27
Scandium propionate complexes
  stability constants, 1A27
Scandium thioglycolate complexes
  stability constants, 1A27
Scandium tricarballylate complexes
  stability constants, 1A27
Scandium trihydroxyisobutyrate complexes
  stability constants, 1A27
Scandium trimethyllactate complexes
  stability constants, 1A27
Scattering
  alkali atom beams with halogens, 8A20
  beta polarization studies, 8A4
  cross sections of isotopic hydrogen mixtures, molecular beam studies, 8A21
  elastic, in crossed alkali metal beams, 5B22
  heavy nuclei, study of level structures by, 8A2
  of high-energy proton beams, 5A26
  studies with charged particles from cyclotrons, 5A34
Scavengers
  effects on radiolysis, 8A33
Scintillation detectors
  amplifier design for, 5A39
  development of low energy, 2A23
  development of new techniques, 8B1
  nuclear spectroscopy, use in, 8A8
Scintillators
  fluorescent decay-time measurements, 7-13
  studies of liquid materials, 2A26
Selenium
  isotope exchange reactions, 8A27
Selenium-79
  decay constants, 2A21
Selenium alloys
  solubility in fused salts, 2B8
Selenium chelates
  reduction studies, 3B8
Selenium isotopes
  separation by isotopic exchange, 8A27
Semiconductor radiation detectors
  beta detection, 8A4
  development, 5A38
  nuclear spectroscopy, use in, 8A8
  proton detection, 8A2
Separations processes
    (See also Fluoride volatility processes, Fused salts, Ion exchange, and Solvent extraction)
  development, 8D1
Settlers
  design of liquid-liquid, 5A68
Silanes
    (See Silicon hydrides)
Silicon
  absorption coefficient measurement, 5B5
  compensated semiconductor detectors, development, 8A2
  semiconductor detectors, surface passivation, 5A38
Silicon-26
  (p,t) reaction, nuclear energy level studies, 5A27
Silicon-32
  half-life measurement, 2A27
Silicon carbide
  enthalpy of formation, 2B11
Silicon fluorides (SiF_4)
  enthalpy of formation, 2B11
Silicon hydrides (Si_2H_6)
  effects of electric discharge on, 5B8
Silicon hydrides (SiH_3PH_2)
  effects of electric discharge on, 5B8
Silicon hydrides ($SiH_3SiH_2PH_2$)
  properties of isomeric forms of, 5B8
Silicon hydrides (SiH_4)
  effects of electric discharge on, 5B8
Silicon ions
  hydrolysis studies, 8A12
Silicon, tetraethyl-
  radiation and photochemistry in benzene and cyclohexane, 7-7
Silver
  isotopic and elemental abundances in meteorites, 2A27
  nuclear magnetic field studies, 5A47
  valence state produced by radiolysis of aqueous solutions, 8A33
Silver-109
  $(p, p\pi^{+})$ reaction, 2A13
Silver chloride
  single crystals, electrical conductivity, 1A23
Sintering
  of thoria gels, 8D14
Sodium (gaseous)
  determination of radiative lifetime in excited state, 5B3
Sodium (liquid)
  solubility of rare gases in, 2B1
Sodium alloys (Bi-Na)
  thermodynamic properties, regenerative cell studies, 2B7
Sodium alloys (K-Na)(liquid)
  thermodynamic properties, 2B2
Sodium alloys (Na-Sn)
  thermodynamic properties, regenerative cell studies, 2B7
Sodium alloys (Na-Te)
  spectrophotometry in fused salt solutions, 2B8
Sodium bromide (liquid)
  phase studies, 2B7
Sodium carbides (Na_2C_2)
  neutron diffraction studies, 2A74
Sodium chloride
  solvent extraction from water, 8A31
Sodium chloride (liquid)
  phase studies, 2B7
Sodium chloride systems ($BaCl_2$-NaCl)
  hydrolytic reactions in aqueous solution, 8A12
Sodium chloride systems (KCl-NaCl)(liquid)
  metal freezing by, in liquid metal extraction studies, 5B19
Sodium chloride systems (LiH-NaCl)
  phase studies, 2B6
Sodium cyanide (liquid)
  phase studies, 2B7
Sodium fluoride (liquid)
  phase studies, 2B7

- Sodium hydroxide (liquid)
  - phase studies, 2B7
- Sodium iodide (liquid)
  - phase studies, 2B7
- Sodium iodide crystals
  - tantalum containing, scintillation properties, 2A23
- Sodium perxenate
  - coprecipitation of radon compound with, 2A68
  - oxidizing agent use in actinide element studies, 2A60
- Sodium phytate
  - neutron diffraction studies of structure, 8A35
- Sodium - sodium bonds
  - energy, 5B15
- Sodium sulfate
  - solubility in water at high temperature, 8C7
- Sodium uranates
  - crystal structure, x-ray diffraction studies, 2A71
- Sodium xenates (Na_4XeO_6)
  - reaction rate with ions in alkaline solution, 5A49
- Solar system
  - nuclear chemistry studies, 5A3
- Solid state physics
  - low temperature calorimetric studies, 2A80
- Solids
  - interaction with gases, molecular beam studies, 2A55
  - magnetic properties, fundamental studies, 1A12
  - radiation chemical studies, 8A34
- Solubility studies
  - of aqueous solutions at high temperature, 8C7
  - intermetallic compounds in fused salts, 2B8
  - oxides in molten salts, 8C9
  - rare gases in liqud alkali metals, 2B1
- Solutions
  - actinide complexes in, 4-3
  - actinide compounds, Raman spectra, 8A1
  - alpha-active, spectrophotometry at high temperatures and pressures, 8D15
  - inorganic ions, separation process development, 8A15
  - metals in molten salts, 8A25
  - polarography of ions and complex compounds in dioxane-water, 7-33
  - spectrophotometry over wide temperature ranges, 8A19
- Solutions (aqueous)
  - actinide complexes in, 4-3
  - corrosion of zirconium alloys, radiation effects, 8C4
  - electrical conductance at high temperature and high pressure, 8C6
  - of electrolytes, thermodynamic data compilation, 6-11
  - high-temperature chemistry, 8C5
  - hydrolytic reactions of inorganic ions, 8A12
  - isopiestic studies at high temperature, 8C8
  - isotope exchange reactions with amalgams, 8A27
  - liquid structure, diffraction studies, 8A24
  - reactions with thorium oxide, 8C3
  - solubility of salts at high temperature, 8C7
  - thermodynamic properties of rare-earth chlorides, 1A13
  - thermodynamic studies on electrolytes, 8A13
- Solvation
  - in solvent extraction, 4-2
  - solvent extraction studies with various ions, 5A50
  - spectrophotometric studies, 8A19
- Solvent extraction
  - (See also Extractants)
  - actinide elements, 2A60
  - of alkali cations using polyiodides, 3B5
  - axial mixing in packed columns, 5A60
  - basic studies, 5A50
  - basic studies, 8D2
  - design of liquid-liquid settlers, 5A68
  - equipment evaluation and development, 8D4
  - fused salt - molten metal system, 1B2
  - liquid-liquid and gas-liquid agitation, 5A65
  - liquid metal systems, 5B19
  - mass transfer from forming and collapsing droplets, 1B1
  - metal nitrates with amines, 8D3
  - methylene blue perchlorate, 3A8
  - molecular interactions, 4-2
  - molten salt systems, 4-1
  - nitric acid reactions with hydrocarbon diluents, 8A31
  - protactinium solution studies, 8D9
  - radiation effects on, 8B4
  - rare earth separation by, 1B8
  - stacked clone contactor development, 8D6
  - systems development, 8D1
  - of thorium by TTA, synergistic effect of tri-n-octylamine, 3B8
  - uranium and thorium ore processing, 8D12
  - use of bifunctional organophosphorus compounds, 1A2
- Solvents
  - (See also Diluents, Extractants, and Organic solvents)
  - interaction with ions, theoretical studies, 2A81
  - nonaqueous, electrochemical studies, 5B30
  - radiation degradation studies, 8D2
  - for rare earth absorption spectra studies, 2A61
- Sound
  - "zero sound" studies in liquid helium-3, 2A79
- Spallation
  - radiochemical studies in targets bombarded with charged particles, 5A24
  - studies with high-energy protons, 2A9
- Spectra
  - (See also Coincidence spectroscopy)
  - of actinides, 5A56
  - of actinides, solid state, 5A55
  - actinide solutions, 4-3
  - analytical methods, 5B4
  - atomic, of configuration interactions, 5A43
  - cation-anion interactions, 2A65
  - deuterium determination in water, 3A13
  - electric resonance, of molecular beams, 5A46
  - of free radicals at cryogenic temperatures, 6-5
  - of free radicals at cryogenic temperatures, 7-25
  - hexafluorides, thermodynamic studies, 2A80
  - of high-temperature systems, 3B1
  - in-beam nuclear, studies of short-lived isotopes, 5A35
  - infrared, of deuterated molecules, 6-8
  - instrument design and development, 5A40
  - of isotopic molecules, 8A26
  - nuclear energy level studies, 8A5
  - paramagnetic resonance, 8A10
  - polymerization studies by, 3B7
  - of protons, using semiconductor detectors, 8A2
  - rare earth atoms and ions, theoretical studies, 2A76
  - spherical nuclei, theoretical calculation comparison with experiment, 5A15
- Spectra (absorption)
  - actinide complexes, 8A1
  - elements from radium through curium, 2A72
  - of free radicals at cryogenic temperatures, 6-5
  - hydrated electron reaction studies, 2A42
  - of rare earth atoms and molecules, 1A8
  - rare earths, 2A61
  - rare earth double nitrates, 2A62
  - solvated electrons in ethanol, 2A41
  - sulfur - nitrogen ions in solution, 5B7
  - transient species in irradiated oxygenated water, 2A45
  - xenon fluorides in hydrogen fluoride and halogen fluoride solutions, 2A67
- Spectra (alpha particles)

  deformed heavy elements, 5A10
  fermium-255, 5A10
  nuclei in transition region between sphericity and strong deformation, 5A9
Spectra (emission)
  analysis by, 2A35
  analytical applications, 1A7
  elements from rodium through curium, 2A72
Spectra (fluorescence)
  rare earths, 2A61
Spectra (gamma radiation)
  deformed heavy elements, 5A10
  nuclei in transition region between sphericity and strong deformation, 5A9
Spectra (infrared)
  acidic organophosphorus compounds, 2A87
  actinide compounds, 8A1
  of complexes containing the P=S bond, 7-31
  of deuterated molecules, 6-8
  dissociation of complexes in solution, studies by, 7-30
  of free radicals at cryogenic temperatures, 6-5
  isotope effects, 3A7
  of isotopic molecules, 8A26
  magnetic materials, 3A12
  metal complexes of dibasic amino acids, 7-39
  protactinium complexes, 8D9
  silicon hydrides, 5B8
  solid inorganic compounds, 2A87
  sulfur trapped in rare gas matrix, 5B4
  transitional metal complexes, 7-39
  uranates, 2A78
  uranium oxides, 2A78
  uranyl salts, 2A78
Spectra (nuclear)
  deformed heavy nuclei, 5A10
  fundamental studies, 3A2
  in-beam observation of short-lived isotopes, 5A35
  nuclei near lead-208, 5A8
  nuclei in transition region between sphericity and strong deformation, 5A9
Spectra (Raman)
  acidic organophosphorus compounds, 2A87
  actinide solutions, 8A1
  isotope effects, 3A7
  of isotopic molecules, 8A26
  magnetic materials, 3A12
  molecular beams, 5B4
  protactinium complexes, 8D9
  solid inorganic compounds, 2A87
  xenon fluorides in hydrogen fluoride and halogen fluoride solutions, 2A67
  xenon hexafluoride using laser light source, 2A66
  yellow solutions using laser light source, 2A67
Spectrometers (mass)
  applications to chemical problems, 8A22
  for charge-neutralization rate studies in ionized gases, 5B14
  design to detect both positive and negative ions, 1A18
  development of two-stage, 2A27
  ion formation in, by electron impact, 5A45
  modulated molecular beam studies, 8A21
Spectrometry
  of beta particles, 2A23
  crystal structure studies, automatic data handling system, 3A12
Spectrometry (absorption)
  alkali metal binary solutions, vapor studies, 2B2
Spectrometry (electrons)
  internal conversion measurements in nuclear level studies, 5A4
  internally converted nuclear transition studies, 5A3
Spectrometry (gamma rays)
  praseodymium decay products, nuclear formation region studies, 5A6
Spectrometry (mass)
  alkali metal compounds ionized from hot filaments, 2A53
  analytical services at BNL, 3A13
  astatine compound identification, 2A59
  bismuth - lithium vapor phase, 2B7
  high sensitivity equipment development, 3A13
  hyperfine structure anomaly studies, 5A13
  fission products, intermediate energy fission studies, 5A22
  of inorganic compounds, physico-chemical characterization by, 1A17, 1A18
  ion reaction studies, 8A34
  ionization of rate gases, experimental threshold laws, 2A85
  neutron cross section measurements by, 3A7
  of products of crossed-beam reactions between atoms and molecules, 2A39
  radon fluorides, 2A58
  rare gas compounds, 2A68
  rare gas measurement after desorption from charcoal, 2B1
  stable isotope detection studies, 5A13
  work functions and ionization potential, measurement by, 5A51
Spectrophotometry
  of alpha-active solutions at high temperatures and pressures, 8D15
  chelates of polyfunctional ligands, 7-35
  intermetallics in fused salts, 2B8
  of metal solutions in molten halides, 3B1
  organogermanium alkoxides, 7-36
  of solutions over wide temperature ranges, 8A19
  solvent extraction studies, 4-2
  uranium isotopes, 2A37
Spectroscopy (optical rotatory dispersion)
    (See Optical rotatory dispersion)
Sputtering
  uranium vaporization for atomic absorption spectrophotometry, 2A37
Spontaneous fission
  half-lives, fundamental studies, 5A18
  fragments, mass and energy distribution studies, 5A19
Stainless steel
  solvent extraction from acid solutions by amines, 8D3
Statistical mechanics
  of dense gases, 6-7
Stereochemistry
  deamination reaction studies, 8A30
  of hydride reduction of organic compounds, 7-28
Stereoisomers
    (See Isomers)
Stilbene
  cis-trans isomerization in benzene, gamma radiation induced, 7-4
  radiation chemical studies of isomers of, 2A40
Stoichiometry
  intermetallics between lanthanide rare earths and group IIB metals, 2B4
Stored energy
  in platinum, effect on catalytic activity, 7-21
Stresses
  in metal oxides from oxygen adsorption, 7-23
Stripping
  general study, 2A1
  heavy nuclei, study of level structures by, 8A2
  rare gases from liquid alkali metals, 2B1
Strontium chloride

- divalent rare earth preparation using, 2A61
- Styrene
  - polymerization, role of ions, 3B7
- Styrene polymers
  - radiation chemistry, 8C1
- Sublimation
  - of graphite, experimental data, 3B2
- Sucrose
  - neutron diffraction studies of structure, 8A35
- Sulfate ion
  - reduction by Desulfovibrio, 5A69
- Sulfides
  - adsorptive properties, 8A23
  - high temperature chemical and physical studies, 2A54
- Sulfonic acids, dinonylnaphthalene-
  - ion exchange studies, 5A50
- Sulfur
  - determination in submilligram samples of organic compounds, 5A71
  - infrared spectra in rare gas systems, 5B4
  - isotope separation by ion exchange, 1A26
  - reactions with nitrogen, 5B7
- Sulfur-35
  - recoil from the $S^{34}(n, r) S^{35}$ reaction, chemical effects, 5A58
- Sulfur chlorides (S_2Cl_2)
  - reactions with ammonia, 5B7
  - reactions with nitrogen, 5B7
- Sulfur - nitrogen compounds (NSCl)
  - preparation, 5B7
- Sulfur - nitrogen compounds (S_3N_2Cl)
  - preparation, 5B7
- Sulfur - nitrogen compounds ($S_3N_2Cl_2$)
  - preparation, 5B7
- Sulfur - nitrogen compounds ($S_4N_3Cl_3$)
  - preparation, 5B7
- Sulfur - nitrogen compounds (S_4N_2)
  - preparation, 5B7
- Sulfur - nitrogen compounds (S_4N_3Cl)
  - preparation, 5B7
- Sulfur - nitrogen compounds (S_4N_4)
  - preparation, 5B7
  - reaction with hydrogen chloride, 5B7
- Sulfur - nitrogen compounds (S_7NH)
  - preparation, 5B7
- Sulfur - nitrogen ions
  - reactions, 5B7
- Sulfur - phosphorus bonds
  - infrared spectra, 7-51
- Sulfur systems (Hf-S)
  - phase relations at high temperature, 1A21
- Sulfuric acid
  - anhydrous, catalytic properties, 5A61
  - corrosion of zirconium alloys, radiation effects, 8C4
  - coulometric generation of Cr^{++} in solutions of, 7-37
  - effects on ion exchange resins, 8D3
  - electrical conductance in water at high temperature and high pressure, 8C6
  - polarographic studies of metal ions in solutions of, 7-37
  - spectrophotometry of solutions over wide temperature ranges, 8A19
- Sun
  - neutrino flux measurements from, 3A4
- Superconductivity
  - phase diagrams for selection of alloy compositions, 5B1
- Surface area
  - of graphites, determination using krypton-85, 3B2
- Surface effects
  - chemical reaction studies, 1A16
  - interactions at metal-gas interfaces, 6-1
  - mass transfer from droplets in solvent extraction, 1B1
  - oxygen adsorption on metal oxides, stresses produced by, 7-23
  - refractory oxides in aqueous media, 8C3
- Surface ionization
  - work functions and ionization potentials, measurement by, 5A51
- Surfaces
  - modulated molecular beam interactions with, 8A21
  - viscoelastic properties, 1A16
- sym-trans-μ-dichloro-dichlorobis(ethylene) diplatinum(II)
  - substitution reaction rates, 1A24
- Tantalum
  - analysis by emission spectrography, 2A35
  - calorimetric studies, 2B13
  - corrosion and film studies in hydrogen fluoride solution, 8A18
  - determination in thorium and rate earths, 1A28
  - diffusion-controlled oxidation, 5B20
  - filament use in surface ionization of alkali metal compounds, 2A53
  - hydrofluoric acid solutions, Raman spectra, 8A1
  - niobium separation by halogenation, 1B9
  - separations by hydrogen peroxide elution, 1A5
  - work-function measurement by surface ionization, 5A51
- Tantalum-181
  - coulomb excitation studies using heavy ions, 5A36
- Tantalum borides (TaB_2)
  - enthalpy of formation, 2B10
- Tantalum carbides (TaC)
  - neutron diffraction studies, 2A74
- Tantalum fluorides (TaF_5)
  - enthalpy of formation, 2B10
- Tantalum halides
  - chemistry of fused, 7X1
- Tantalum ions
  - hydrolysis studies, 8A12
- Tartaric acid complexes
  - optical rotatory dispersion studies, 2A57
- Technetium
  - nuclear and inorganic chemistry, 8A9
  - separation from fission products, 8A9
- Technetium compounds
  - thermodynamic properties, measurement, 8A11
- Technetium fluorides (TcF_6)
  - low temperature calorimetric studies, 2A80
  - quantum mechanical studies of electronic-nuclear interactions, 2A75
- Tellurium
  - isotope exchange reactions, 8A27
- Tellurium-131
  - isomer yields in fission, 2A14
- Tellurium alloys
  - solubility in fused salts, 2B8
- Tellurium alloys (Li-Te)
  - spectrophotometry in fused salt solutions, 2B8
- Tellurium alloys (Na-Te)
  - spectrophotometry in fused salt solutions, 2B8
- Tellurium bromides ($TeBr_4$)
  - structure, 1A11
- Tellurium chlorides ($TeCl_4$)
  - structure, 1A11
- Tellurium isotopes
  - separation by isotopic exchange, 8A27
- Temperature
  - (See also High-temperature chemistry, High-temperature facilities, and Low-temperature research)
  - determination in metals under high pressure by resistivity changes, 5B10

  effects on absorption spectra of sodium vapor, 2B2
  2B1
  effects on coordination number of metal ions in fused *salt solutions*, 2A63
  effects on enzyme reactions, 3A11
  effects on liquid structure of water, nuclear magnetic resonance studies, 2A84
  effects on ion exchangers, 8D8
  effects on proton resonance in electrolyte solutions, 2A84
  effects on radiolysis, 8A33
  effects on rare gas solubility in liquid alkali metals,
  gradient measurement in thermal insulators at high pressure, 5B12
Terbium
  absorption spectra in oxy-acetylene flames containing ethanol solutions of perchlorates, 1A8
  bombardment by neon-22 ions to produce rhenium-181, 5A21
  isolation by ion exchange, 1A25
Terbium-159
  coulomb excitation studies using heavy ions, 5A36
  production by high energy proton reactions, 2A16
Terbium carbides (Tb_3C)
  neutron diffraction studies, 2A74
Terbium intermetallic compounds ($TbNi_2$)
  neutron diffraction studies, 3A12
Terphenyl
  solutions in aliphatic alcohols, solvated electron studies, 2A41
Terphenyl, 4-bromo-p-
  luminescence in benzene, decay time, 7-10
Tetrachlorodiphenyl
  separation from water, design of liquid-liquid settler, 5A68
Tetraethyl lead
    (See Lead, tetraethyl-)
Tetraethyl silicon
    (See Silicon, tetraethyl-)
Tetrafluoromethane
    (See Carbon tetrafluoride)
1,4,5,8-tetrahydronaphthalene
    (See Naphthalene, 1,4, 5,8- tetrahydro-)
Tetranitro methane
  pulse radiolysis of solutions of, 2A44
Thallium
  valence state produced by radiolysis of aqueous solutions, 8A33
Thallium-204
  fission barrier measurements, 5A16
Thallium alloys (Tl-U)(liquid)
  thermodynamic properties, 2B3
Thallium chlorides
  thermodynamic properties, 3A8
Thallium ions
  exchange, effects of chloride ions, 3A8
  oxidation of chromium ions, effects of chloride ions, 3A8
Thallium isotopes
  isomers, study by in-beam spectroscopy, 5A35
Thallium systems (Sn-Tl)
  liquid, thermodynamic properties, 1B4
Theoretical nuclear chemistry
  computer calculations of the pairing Hamiltonian, 2A69
Theoretical organic chemistry
  structure studies, 3A9
Thermal conductivity
  insulators, effects of high pressure, 5B12
Thermal decomposition
    (See Pyrolysis)
Thermal insulation
    (See Insulation (thermal))
Thermal spikes
  radiolysis studies, LET effects, 8A34
Thermal transpiration
  studies on gases, 8C11
Thermochemistry
    (See also Calorimetry, Thermodynamics, etc.)
  diborides of Group IV and V metals, 2B10
  of lanthanides and actinides, 5A53
  uranium compounds, 2B12
Thermodynamics
    (See also specific thermodynanic properties, e.g., Entropy, Free energy, etc.)
  alkali metal binary solutions, 2B2
  aqueous electrolytes solutions, 8A13
  of aqueous salt solutions at high temperature, 8C7
  of aqueous systems at high temperature and high pressure, 8C6
  binary alloy systems, 2B7
  data collection, analysis, and compilation, 6-11
  data compilation for metal oxides and halides, 5B2
  of fluoride gases, 6-6
  of gases, infrared spectroscopic studies, 6-8
  heat transfer data interpretation, 5B28
  high temperature molecules, 5B5
  of high-temperature vaporization, 1A21
  liquid metal binary solutions, 2B3
  of liquid metals, 1B4
  lithium hydride systems, 2B6
  low temperature calorimetric studies, 2A80
  mass transfer data interpretation, 5B28
  materials at high temperatures, 2A54
  of metal-alloy and fused-salt solutions, 5A62
  metals under high pressure, 5B10
  physical chemistry of gaseous working fluids, 8C11
  of rare-earth chloride solutions, 1A13
  rare gases, determination from solubility in liquid alkali metals, 2B1
  synthetic organic ion exchangers, 8A14
  thallium chlorides, 3A8
  transition elements and compounds, 8A11
  vaporization process, 2A55
Thermogravimetry
  chelates of polyfunctional ligands, 7-35
Thiocyanates
  spectroscopic studies of characteristic vibrations, 1A8
Thiolperoxides
  chlorinolysis, stereochemical and isotopic studies, 8A36
Thoria gels
  sintering and surface properties, 8D14
Thorium
  compounds, low temperature calorimetric studies, 2A80
  emission spectroscopy, 2A72
  fluorometric determination, 7-38
  nuclear energy level studies, 8A2
  ore reserves and process costs, 8D10
  oxygen and nitrogen determination in, 1A6
  recovery from rocks, geologic aspects, 8D11
  separation from uranium by solvent extraction, 8A31
  solvent extraction by TTA, synergistic effect of tri-n-*octylamine*, 3B8
  tantalum determination by activation analysis, 1A28
Thorium-229
  decay scheme, 2A22
  decay studies, 2A23
  fission, mass distribution studies, 2A14
  neutron cross sections, 2A8
Thorium-230
  coulomb excitation studies using heavy ions, 5A36
  neutron cross sections, 2A8

- Thorium-232
  - decay constants, 2A21
- Thorium carbides
  - preparation and properties, 8D13
- Thorium fluoride
  - radiolysis, 8C2
- Thorium iodides
  - physical and chemical properties, 1A19
- Thorium iodide systems (Th-ThI$_4$)
  - physical and chemical properties, 1A19
- Thorium ions
  - hydrolysis at high temperature, 8C5
  - hydrolysis studies, 8A12
- Thorium ores
  - processing techniques, improvement, 8D12
- Thorium oxide
  - gels and sols, preparation and properties, 8D13
  - reactions with water and aqueous solutions, 8C3
- Thorium oxyiodide
  - formation in the Th-ThI$_4$ system, 1A19
- Thorium sulfide systems (ThS-US)
  - magnetic susceptibility determination, 2B5
- Thorium systems (Th-ThI$_4$)
  - physical and chemical properties, 1A19
- Thulium
  - bombardment by carbon-12 ions to produce rhenium-181, 5A21
  - isolation by ion exchange, 1A25
- Thulium-169
  - coulomb excitation studies using heavy ions, 5A36
- Thulium intermetallic compounds (TmMn$_2$)
  - neutron diffraction studies, 3A12
- Thulium oxides (Tm$_2$O$_3$)
  - phase studies at high temperatures and pressures, 2A56
- Thymine
  - absorption spectra of hydrated electrons in aqueous solutions of, 2A43
- Tin-119
  - Mossbauer effect in complexes of, 7-29
- Tin-132
  - nuclei near to, decay schemes of, 5A7
- Tin alloys
  - solubility in fused salts, 2B8
- Tin alloys (Li-Sn)
  - thermodynamic properties, regenerative cell studies, 2B7
- Tin alloys (Na-Sn)
  - thermodynamic properties, regenerative cell studies, 2B7
- Tin alloys (Sn-U)(liquid)
  - thermodynamic properties, 2B3
- Tin, bis(8-quinolinato)
  - Mossbauer effect in, 7-29
- Tin complexes
  - Mossbauer effect in, 7-29
- Tin systems (Sn-Tl)
  - liquid, thermodynamic properties, 1B4
- Tin systems (Sn-Zn)
  - liquid, distillation studies, 1B5
- Tin, tetraethyl-
  - radiation and photochemistry in benzene and cyclohexane, 7-7
- Titanium
  - fluorometric determination, 7-38
- Titanium-42
  - search for, 3B10
- Titanium borides (TiB$_2$)
  - enthalpy of formation, 2B10
- Titanium carbides (TiC)
  - neutron diffraction studies, 2A74
- Titanium fluorides (TiF$_4$)
  - enthalpy of formation, 2B10
- Titanium uranates
  - crystal structure, x-ray diffraction studies, 2A71
  - uranium-oxygen bond studies, 2A78
- Titrators
  - development of conductometric, 8B3
- Tributylphosphate systems (TBP-UO$_2$(NO$_3$)$_2$-H$_2$O)
  - activity measurements, 8D2
- Toluene
  - radiation-induced reactions, 3B7
- p-Toluidine
  - complexes with metal halides, dissociation in solution, 7-30
- Tracer studies
  - carbon-14 labeled tetraalkyl ammonium ion, ion exchange studies, 8A14
  - corrosion inhibitors, use of chromium-51, 8A16
  - learning process in planarians, 3A11
  - liquid metal extraction kinetics, 5B19
  - oxygen-18 in water radiolysis studies, 8A33
- Transfer reactions
  - general study, 2A1
- Transition metals
  - bromates of, spectral studies, 2A87
  - carbonates of, spectral studies, 2A87
  - complexes, infrared spectra, 7-39
  - complexes, reaction kinetics, 1A15
  - coordination number in fused salt solutions, 2A63
  - iodates of, spectral studies, 2A87
  - nitrates of, spectral studies, 2A87
  - phase diagrams, 5B1
  - thermodynamic studies, 8A11
- Transplutonium elements
  - preparation and properties, 5A54
  - separations chemistry, 2A90
- Transuranium elements
  - spectrophotometry of solutions at high temperatures and pressures, 8D15
- Tri-n-octylamine
  - synergistic effect in solvent extraction of thorium, 3B8
- Tributylphosphate systems (HNO$_3$-TBP-H$_2$O)
  - activity measurements, 8D2
- Tributylphosphine sulfide
  - infrared spectra, 7-31
- Trichloroammineplatinate (II) ions
  - substitution reaction rates, 1A24
- Trifluoromethane
  - (See Methane, trifluoro-)
- Trifluoromethyl radical
  - isotope effects in kinetics of hydrogen abstraction reactions, 3A7
- Tripiperidinophosphine sulfide
  - infrared spectra, 7-31
- Triphenyl aluminum
  - structure, 1A11
- Tripyrrolidinophosphine sulfide
  - infrared spectra, 7-31
- Tritium
  - beta spectrum studies, 2A23
  - production by fission, scintillator studies, 2A26
  - recoil from nuclear reactions, chemical effects, 5A58
- Tritons
  - isotope production by, 3B10
- Tungstates
  - ion exchange and adsorption properties, 8A23
- Tungsten
  - analysis by emission spectrography, 2A35
  - calorimetric studies, 2B13
  - diffusion-controlled oxidation, 5B20
  - energy levels in the rotational region, 5A35
  - filament use in surface ionization of alkali metal

    - compounds, 2A53
  - fluorometric determination, 7-38
  - separations by hydrogen peroxide elution, 1A5
  - work-function measurement by surface ionization, 5A51
- *Tungsten-187*
  - exchange between metatungstate polymers and orthotungstate, 1A22
- Tungsten ions
  - hydrolysis studies, 8A12
- Tungsten isotopes
  - hyperfine structure studies, 5A13
- Turbulence
  - wall effects in fluid flow, 5A70
- Tyrosine
  - metal complexes, infrared spectra, 7-39
- Ultracentrifugation
  - deuteriated proteins, 2A52
- *Ultraviolet radiation*
  - decay-time of luminescence excited by, 7-10
  - *design of accurately reproducible source, 7-9*
  - effects on xylene isomers, 2A48
  - photochemical studies, 8A34
  - photochemistry, 6-3
  - photochemistry of organometallics, 7-3
  - radiation chemical studies using organic compounds, 2A40
- Uranates
  - crystal structure, x-ray diffraction studies, 2A71
  - preparation in fused salt solutions, 2A62
  - uranium-oxygen bond studies, 2A78
- Uranium
  - *atomic spectra studies, 5A56*
  - chronopotentiometry in molten fluorides, 8B2
  - compounds, calorimetric determination of enthalpy of formation, 2B12
  - compounds, low temperature calorimetric studies, 2A80
  - emission spectroscopy, 2A72
  - ionization-potential measurement by surface ionization, 5A51
  - ions, solid state spectra studies, 5A55
  - irradiation with helium ions and deuterons, 2A1
  - isotopic analysis by atomic absorption spectrophotometry, 2A37
  - nuclear energy level studies, 8A2
  - *recovery from irradiated fuels, 3B4*
  - separation from thorium by solvent extraction, 8A31
  - *fission, tellurium isomer yields, 2A14*
- Uranium-234
  - *coulomb excitation studies using heavy ions, 5A36*
- Uranium-235
  - alpha particle irradiations, 2A1
  - coulomb excitation studies using heavy ions, 5A36
  - decay constants, 2A21
  - fission properties, 2A20
  - fission, tellurium isomer yields, 2A14
  - near-threshold fission, 2A15
- Uranium-235m
  - decay energy, calorimetric determination, 5A12
- Uranium-236
  - abundance in natural uranium, 2A27
  - coulomb excitation studies using heavy ions, 5A36
  - *decay constants, 2A21*
  - fission by high-energy protons, 2A9
  - fission studies with high-energy helium ions, 2A19
  - abundance measurements of uranium-236 in, 2A27
- Uranium alloys (Cd-U)(liquid)
  - thermodynamic properties, 2B3
- Uranium alloys (Cr-U)(liquid)
  - liquid metal extraction studies using, 5B19
- Uranium alloys (Ga-U)(liquid)
  - thermodynamic properties, 2B3
- Uranium alloys (In-U)(liquid)
  - thermodynamic properties, 2B3
- Uranium alloys (Pb-U)(liquid)
  - thermodynamic properties, 2B3
- Uranium alloys (Sn-U)(liquid)
  - thermodynamic properties, 2B3
- Uranium alloys (Tl-U)(liquid)
  - thermodynamic properties, 2B3
- Uranium alloys (U-Zn)(liquid)
  - thermodynamic properties, 2B3
- Uranium carbides
  - preparation and properties, 8D13
- Uranium carbides (UC_2)
  - vaporization, thermodynamic studies, 2A55
- Uranium chloride systems ($KCl-LiCl-UCl_4$)(liquid)
  - chlorination rate of uranium tetrachloride in, 5B18
- Uranium chlorides (UCl_4)
  - reaction rate with chlorine, 5B18
- Uranium fluorides (UF_4)
  - *enthalpy of formation, 2B12*
  - radiolysis, 8C2
- Uranium hydrides (UH_3)
  - low temperature calorimetric studies, 2A80
- Uranium intermetallic compounds (UCd_{11})
  - magnetic susceptibility, 2A83
- Uranium ores
  - processing techniques, improvements, 8D12
- Uranium oxides
  - crystal structure, x-ray diffraction studies, 2A71
  - gels and sols, preparation and properties, 8D13
- Uranium oxides (UO_2)
  - phase studies at high temperatures and pressures, 2A56
  - stoichiometry, radiation effects, 8B4
- Uranium oxides (UO_{2+x})
  - free energy measurements at high temperatures, 2A54
- Uranium oxides (UO_3)
  - phase studies at high temperatures and pressures, 2A56
  - uranium-oxygen bond studies, 2A78
- Uranium oxides (U_3O_7)
  - crystal structure, neutron and x-ray diffraction studies, 2A71
  - phase studies at high temperatures and pressures, 2A56
- Uranium phosphides
  - enthalpy of formation, 2B12
- Uranium sulfides
  - *enthalpy of formation, 2B12*
- Uranium sulfides (US)
  - *magnetic susceptibility determination, 2B5*
- Uranium sulfides, systems (ThS-US)
  - *magnetic susceptibility determination, 2B5*
- Uranium systems (O-U)
  - phase studies at high temperatures and pressures, 2A56
- Uranyl borate
  - crystal structure, x-ray diffraction studies, 2A71
- Uranyl borates ($UO_2B_2O_4$)
  - uranium-oxygen bond studies, 2A78
- Uranyl ions
  - hydrolysis at high temperature, 8C5
  - reduction kinetics, 8C4
- Uranyl nitrate systems ($TBP-UO_2(NO_3)_2-H_2O$)
  - *activity measurements, 8D2*
- Uranyl sulfate solutions
  - corrosion of zirconium alloys, radiation effects, 8C4
- Vacuum techniques
  - analysis of submilligram organic samples, 5A71
- Valences
  - covalence of inorganic salts, spectral studies, 2A87
  - of transplutonium metals, 5A54
- Vanadium
  - oxygen and nitrogen determination in, 1A6

Vanadium-51
  radioactive decay studies, 8A5
Vanadium ions
  oxidation kinetics, 1A15
Vanadium uranates
  uranium-oxygen bond studies, 2A78
Vapor phase chromatography
  (See Chromatography (vapor phase))
Vapor pressure
  alkali metal binary solutions, thermodynamics studies, 2B2
  americium dioxide, 2A60
  curium dioxide, 2A60
  of molten salts, measurements, 8C9
Vaporization
  sodium, enthalpy determination, 2B2
  thermodynamic studies, 2A55
Vibrations
  "zero sound" studies in liquid helium-3, 2A79
Vic-dioximes
  chemical studies, 1A3
Viscosity
  liquid helium-3 at low temperatures, 2A79
  of molten salts, measurements, 8C9
Volatilization
  heavy element separation techniques, 5A5
Voltammeter
  development for molten-salt applications, 8B3
Water
  corrosion of zirconium alloys, radiation effects, 8C4
  deuterium determination by spectroscopy, 3A13
  effects in solvent extraction, nuclear magnetic resonance studies, 5A50
  exchange rate between hydrated ions and solvent, 2A84
  hydration of metal ions, kinetic and stoichiometric studies, 5B6
  hydroxyl radical absorption in, 2A44
  infra-red spectra, electrolyte effects, 8A19
  interactions with ions, theoretical studies, 2A81
  liquid structure, diffraction studies, 8A24
  oxygenated, pulse radiolysis studies, 2A45
  pulse radiolysis studies, 2A44
  radiation chemistry of, 3A5
  radiolysis mechanism, scavenger and tracer studies, 8A33
  reactions with thorium oxide, 8C5
  structure, nuclear magnetic resonance studies, 2A84
  substitution rates in platinum complexes, 1A24
  synthesis from hydrogen and oxygen, effects of carbon dioxide and rare gases, 8A34
  transient conductivity after pulse irradiation, 2A46
Water (D_2O)
  effects on photosynthesis, 2A51
  growth of lower plants in, 2A50
  infra-red spectra, electrolyte effects, 8A19
  solvent use in studies of inter- and intra-molecular hydrogen bonding, 2A82
Wilson G-F Matrix
  metal-nitrogen bond stretching constant studies, 7-39
Work functions
  measurements by surface ionization studies, 5A51
X-radiation
  from fission reactions, 2A14
  line broadening studies of thoria gels, 8D14
  relation to fragment mass in prompt fission, 5A17
X-ray diffraction analysis
  actinide compounds, 4-3
  atomic charge studies, 3A12
  barium titanates, 2A71
  cesium cadmium chlorides, 2A71
  computer applications, 1A10
  crystal structure studies, 5A41
  high temperature phase studies, 2A54
  liquid structure studies, 8A24
  metal- molten salt solutions, 8A25
  phase studies of lanthanide rare earth-group IIB intermetallics, 2B4
  potassium praseodymium nitrates, 2A71
  structure of Yang's molecule, 3A9
  uranate crystal structure studies, 2A71
  uranium oxides, 2A71
  uranyl borate, 2A71
Xenon
  chemical properties, 5A49
  compounds with fluorine, radiation chemistry, 3B3
  diffusion studies, 8C11
Xenon fluoride systems ($BF_3 \cdot XeF_6$)
  complex formation in xenon fluoride studies, 2A66
Xenon fluorides
  hydrolysis products, 2A66
  isotope effects, spectroscopic studies, 8A26
  mass spectrometry, 2A68
Xenon fluorides (XeF_2)
  formation, photochemical studies, 2A47
  hydrolysis in acidic and alkaline solutions, 5A49
  low temperature calorimetric studies, 2A80
Xenon fluorides (XeF_4)
  hydrolysis in acidic and alkaline solutions, 5A49
  low temperature calorimetric studies, 2A80
Xenon fluorides (XeF_6)
  chemical properties, 2A66
  low temperature calorimetric studies, 2A80
  magnetic susceptibility, 2A83
  molecular structure studies, 2A66
  neutron diffraction studies of structure, 8A35
  quantum mechanical studies of electronic-nuclear interactions, 2A75
  Raman spectra studies using laser light source, 2A66
Xenon ions
  stability in aqueous solutions, 5A49
Xenon oxides (XeO_3)
  disproportionation in alkaline solutions, 5A49
  reaction rate with various ions in acidic solution, 5A49
Xenon oxides (XeO_4)
  mass spectrometry, 2A68
Xenon oxyfluorides
  mass spectrometry, 2A68
Xenon resonance lamps
  development, 6-3
Xylene
  radiation-induced reactions, 3B7
  gamma ray radiolysis of isomers of, 2A48
Yang's molecule
  structural studies by x-ray diffraction, 3A9
Yeasts
  growth in heavy water, 2A50
Ytterbium
  energy levels in the rotaional region, 5A35
Ytterbium oxides (Yb_2O_3)
  phase studies at high temperatures and pressures, 2A56
Yttrium
  reaction with its molten chloride and iodide, 1A20
  surface reactions with chlorine, 6-1
Yttrium benzilate complexes
  stability constants, 1A27
Yttrium 2,3-dihydroxy-2-methylbutyrate
  stability constants, 1A27
Yttrium glycolate complexes
  stability constants, 1A27
Yttrium hydroxyisobutyrate complexes
  stability constants, 1A27

Yttrium isobutyrate complexes
    stability constants, 1A27
Yttrium lactate complexes
    stability constants, 1A27
Yttrium methoxyacetate complexes
    stability constants, 1A27
Yttrium propionate complexes
    stability constants, 1A27
Yttrium thioglycolate complexes
    stability constants, 1A27
Yttrium tricarballylate complexes
    stability constants, 1A27
Yttrium trihydroxyisobutyrate complexes
    stability constants, 1A27
Yttrium trimethyllactate complexes
    stability constants, 1A27
Zachariasen rule
    uranium-oxygen bond studies, 2A78
Zeeman *effect*
    elements from radium through curium, 2A72
Zinc
    isotope exchange reactions, 8A27
    muon reactions, radiochemical studies, 2A12
Zinc alloys (Ce-Zn)(liquid)
    phase studies, 2B4
Zinc alloys (La-Zn)(liquid)
    phase studies, 2B4
Zinc alloys (Nd-Zn)(liquid)
    phase studies, 2B4
Zinc alloys (Pr-Zn)(liquid)
    phase studies, 2B4
Zinc alloys (Pu-Zn)(liquid)
    thermodynamic properties, 2B3
Zinc alloys (U-Zn)(liquid)
    thermodynamic properties, 2B3
Zinc halides
    chemistry of fused, 7X1
    complexes with aryl amines, dissociation in solution, 7-30
Zinc ions
    absorption spectra of hydrated electrons in aqueous solutions of, 2A43
    complexes with dibasic amino acids, infrared spectra, 7-39
    complexes with DL-leucine, infrared spectra, 7-39
    complexes with DL-norvaline, infrared spectra, 7-39
    complexes with DL-phenylalanine, infrared spectra, 7-39
    half-wave potential and diffusion current in solutions, 7-33
Zinc oxide systems (Cr_2O_3-ZnO)
    diffusion studies, 7-24
Zinc oxide systems (Fe_2O_3-ZnO)
    diffusion studies, 7-24
Zinc systems (Sn-Zn)
    liquid, *distillation studies*, 1B5
Zinc uranates
    crystal structure, x-ray diffraction studies, 2A71
    uranium-oxygen bond studies, 2A78
Zirconium
    corrosion and film studies in hydrogen fluoride solution, 8A18
    solvent extraction from acid solutions by amines, 8D3
Zirconium-90
    nuclei near to, decay schemes of, 5A7
Zirconium alloys
    aqueous corrosion, radiation effects, 8C4
Zirconium borides (ZrB_2)
    enthalpy of formation, 2B10
Zirconium fluorides (ZrF_4)
    enthalpy of formation, 2B10
    radiolysis, 8C2
Zirconium phosphate
    separation of transplutonium elements by gels of, 2A90

AUTHOR INDEX

A

Abbink, Henry, 1A23
Abbink, J., Jr., 1A5
Abraham, B. M., 2A79, 2A80
Abraham, M., 5A52
Ackermann, R. J., 2A54, 2A55
Adams, John S., 8D11
Agron, P. A., 8A35
Allen, A. O., 3A5
Anbar, M., 2A42, 2A43
Anderson, A., 1A18
Anderson, David, 5A31
Antoun, M. Lawreace, 7-37
Appelman, E. H., 2A59
Arai, S., 2A41
Arakawa, T., 7-3
Asaro, F., 5A8, 5A9, 5A10
Atoji, M., 2A74
Auerbach, Clemens, 3B9
Ausloos, Pierre, 6-2

B

Baes, C. F., 8C9
Baes, C. F., Jr., 8C5
Bailey, Barbara, 5A12
Baldock, C. R., 8A22
Baldwin, W. H., 8A31
Ballantine, D. S., 3B7
Banchero, J. T., 7-21
Banks, Charles V., 1A1, 1A2, 1A3
Bansal, B. M. L., 5A42
Barling, M. M., 1A3
Barnes, R., 2A1
Barnes, R. J., 2A8
Bartell, L. S., 1A9
Basile, L. J., 2A90
Beck, A., 5A50
Begun, G. M., 8A26
Benioff, P., 2A70
Benjamin, B. M., 8A29, 8A30
Benson, James E., 1A10
Bigeleisen, J., 3A7
Biggers, R. E., 8D15
Binau, Douglas E., 1A15
Birk, James P., 1A15
Blake, C. A., 8D1
Blumenberg, W., 1B7
Boesiger, D., 1B9
Bottei, R. S., 7-35, 7-36, 7-37, 7-38
Bowman, H. R., 5A17
Boyd, G. E., 8A9, 8A14, 8A32
Boyd, M., 6-7
Boyle, J. W., 8A33, 8A34
Bredig, Max A., 8A24, 8A25
Breivogel, W., 5A46
Brenner, Abner, 6-9, 6-10
Brewer, Leo, 5B1, 5B2, 5B3, 5B4, 5B5
Brosi, A. R., 8A4, 8A8
Brown, G. M., 8A35
Brown, K. B., 8D1, 8D10, 8D12
Brown, R., 1A5
Brown, W. G., 2A40
Brugger, J. E., 2B13
Bucher, J., 5A50
Buck, W. L., 2A46
Buell, Charles, 1B5
Burde, J., 5A35
Burer, T., 2A57
Burger, L. L., 4-1, 4-2, 4-3
Burkhart, Lawrence, 1B1, 1B2, 1B3
Burkholder, Harvey, 1A25
Burnet, George, 1B4, 1B5, 1B6
Burnett, J., 5A53, 5A54
Burton, Milton, 7-1, 7-2, 7-3, 7-4, 7-6, 7-8, 7-9, 7-10, 7-11, 7-12, 7-13, 7-14
Busey, R. H., 8A9, 8A11
Busing, W. R., 8A35
Byers, C. H., 5A74

C

Cafasso, F., 2B2, 2B5
Cafasso, F. A., 2A83
Campbell, D. O., 8D9
Cantor, S., 8C9
Capellen, J., 1A17
Cartledge, George H., 8A16
Carnall, W. T., 2A60, 2A61, 2A62
Catey, Sara L., 6-9
Cathers, G. I., 8D16
Caton, J. E., Jr., 1A3
Cerny, J., 5A27, 5A28
Chackalackal, Scaria M., 7-30
Chasanov, M. G., 2B3
Chasman, R. R., 2A69
Chaudhri, Man Mohan, 1A16
Chen, J. C., 3A10
Chernick, C. L., 2A66
Chester, C. F., 8D5
Chetham-Strode, A., 8A1, 8A2
Christman, D., 3A13
Chutjian, A., 5B3
Claassen, H., 2A66
Clark, D. E., 1A29

Clark, M. W., 5A65
Clark, R. G., 1A28
Clarke, John, 3B2
Clarkson, J. E., 5A6
Cohen, D., 2A60, 2A61, 2A62
Coleman, C. F., 8D1
Collins, C. J., 8A28, 8A29, 8A30
Connick, R. E., 5B6
Conrad, E., 1A8
Conway, J., 1B9
Conway, J. G., 5A55, 5A56
Conzemius, R., 1A18
Conzemius, R. J., 1A17
Conzett, H. E., 5A25, 5A26, 5A34
Cooper, J. A., 5A7
Corbett, J. D., 1A19, 1A20
Corliss, L. M., 3A12
Coughlen, T. D., 5A65
Craig, C. A., 2A82
Crespi, H. L., 2A50, 2A51, 2A52
Crouse, D. J., 8D1, 8D10, 8D12
Crouthamel, C. E., 2B6, 2B7, 2B8, 2B9
Crowe, W., 1B7
Cumming, J., 3A1
Cunningham, B. B., 5A42, 5A52, 5A53, 5A54
Curran, Columba, 7-29, 7-30, 7-31, 7-33, 7-39
Czapski, G., 2A45

D

Dahmer, L., 1A5
Dale, J. M., 8B2
D'Alessio, A., 7-38
D'Alessio, J. T., 7-9, 7-10
Dallmann, W., 1A6
Darriulat, P., 5A30, 5A32
Datz, S., 8A20, 8A21
Davis, R., 3A3
Davis, R., Jr., 3A4
Davis, R. M., 5A70
Davis, Wallace, Jr., 8D2, 8D8
Dawson, Peter, 1A16
Day, P., 2A24, 2A25, 2A77
Deters, J. F., 7-34
DeVries, D. B., 1A29
Dhar, S. K., 2B1
Diamond, H., 2A7, 2A8, 2A20
Diamond, R. M., 5A35, 5A36, 5A50
Dibeler, Vernon H., 6-4
Dillon, M. A., 7-8, 7-10, 7-11, 7-13
Dodson, R. W., 3A8
Dorfman, L. M., 2A41, 2A45
Drury, J. S., 8A26, 8A27
Durkin, J. A., 7-39

E

Eckstein, Y., 2A79
Edwards, V., 5A69
Egan, J. J., 3B1
Ehrenson, S., 3A9
Eichler, E., 8A3
Elder, J., 2B9
Eliel, E. L., 7-27, 7-28
Elliott, N., 3A12
Ellison, R. D., 8A35
Engelkemeir, D. W., 2A22
Espenson, James H., 1A15
Evans, W. H., 6-11

F

Fahien, R., 1B7
Fahsel, Michael J., 1A1
Fajer, Jack, 3B8
Faltens, M. A., 5A48
Fangman, T., 7-35
Faris, J., 2A35
Farrell, J., 1A27
Fassel, Velmer A., 1A6, 1A7, 1A8
Feder, H. M., 2B1, 2B2, 2B5
Feldberg, Stephen, 3B9
Felt, Rowland, 1B2
Ferguson, J. W., 1A2
Ferraro, John R., 2A87
Fields, P. R., 2A1, 2A7, 2A8, 2A20, 2A58, 2A60, 2A61, 2A62
Fisher, D. J., 8B3
Fitzwater, Donald R., 1A10, 1A11
Flesch, G. D., 1A17, 1A18
Flotow, H. E., 2A80
Flynn, K., 2A18
Flynn, K. F., 2A14, 2A21
Forrester, J. D., 5A41
Foster, M. S., 2B7, 2B8
Frame, H. D., 2A32
Frankel, R. B., 5A1, 5A48
Franzen, Hugo F., 1A21
Fred, M., 2A72
Fredrickson, D. R., 2B13
Freed, S., 3A11
Freedman, M. S., 2A22, 2A23
Fricke, H., 2A42
Friedlander, G., 3A1
Friedman, A. M., 2A1, 2A7, 2A20
Friedman, L., 3A10, 3A13
Fritz, James, 1A4, 1A5
Fuchs, L., 2A30, 2A56
Fueki, Kenji, 7-18, 7-19
Funabashi, Koichi, 7-20

G

Gallivan, J. B., 7-16
Garrison, Warren M., 5A77
Gerstein, Bernard C., 1A12, 1A14
Ghiorso, A., 5A5
Ghormley, J. A., 8A33, 8A34
Giacchetti, A., 2A72
Gibbon, Charles, 7-22
Gilat, J., 5A23
Gindler, J., 2A22
Gindler, J. E., 2A18
Glendenin, L. E., 2A14, 2A21
Glendenning, N. K., 5A15, 5A37
Gmitro, J., 5A61
Goleb, J. A., 2A37
Goodman, G. L., 2A75
Gordon, S., 2A42, 2A43
Goto, Totaro, 1B8

Goulding, F. S., 5A38, 5A39
Green, J., 5A42, 5A54
Green, M., 6-7
Greenberg, E., 2B10, 2B11
Greene, R., 1A5
Grens, E., 5B28
Griffin, H. C., 2A14
Grossmann, W., 1A7
Grover, J. R., 3A1
Gruen, D. M., 2A63, 2A83, 2B5
Gruenhut, E., 7-13
Guenther, R. A., 2A79
Gulyas, E., 2A57, 2A65
Gupta, A., 1A27
Gutmacher, R. G., 5A56

H

Hadeishi, T., 5A72
Halberg, M., 1B7
Halow, I., 6-11
Halperin, Joseph, 8A7
Hamill, W. H., 7-15, 7-16
Hamilton, W. C., 3A12
Hansen, Robert S., 1A16
Hansen, W. L., 5A38
Hanson, D. N., 5A66
Harbottle, G., 3A6
Harmer, D. S., 3A4
Hart, E. J., 2A42, 2A43
Harvey, B. G., 5A28, 5A33, 5A34
Hastings, J. M., 3A12
Hauge, R., 5B4, 5B5
Hauser, W. P., 7-15
Hausman, E. D., 5A75
Hebert, A., 5A46
Hedrick, Edward, 1A4
Heidberg, J., 2A73
Heinrich, R., 2B6
Hennico, A. N., 5A60
Hennion, G. F., Jr., 7-15
Herbst, J. A., 7-21
Heuss, J., 5A67
Higgins, C. E., 8A31
Hillman, Manny, 3B10
Hilsenrath, Joseph, 6-6
Hindman, J. C., 2A84
Hirschmann, R., 1A8
Hochanadel, C. J., 8A33, 8A34
Hoekstra, H., 2A56
Hoekstra, H. R., 2A78
Hollander, J. M., 5A3, 5A4, 5A7
Hollowell, C., 5A46
Holman, Kermit, 1B3
Holt, B. D., 2A36
Hooper, R. J., 7-39
Hooten, Norris, 7-23
Horen, D. J., 5A33
Horrocks, D. L., 2A26, 2A68
Horwitz, E. P., 2A90
Hu, A., 2B13
Hu, John, 7-26
Huang, Robert, 1B3
Hubbard, W. N., 2B10, 2B11, 2B12, 2B13
Huff, E., 2A35
Huizenga, J. R., 2A2, 2A3, 2A4, 2A5, 2A6, 2A15, 2A18, 2A19
Hung, Tsu-Chang, 8A33, 8A34
Hutchison, D. A., 2A85
Hyde, E. K., 5A11, 5A23, 5A24
Hyder, M. L., 5A58
Hyman, H. H., 2A66, 2A67

I

Ibers, J. A., 3A12
Igo, G. J., 5A34
Igo, George, 5A30, 5A32
Ingalls, R. B., 7X2

J

Jackovitz, J. F., 7-39
Jacobsen, E. C., 1A28
Jaffey, A., 2A21
Jeannin, Yves P., 1A11
Jelinek, Frank, 1A12
Jenks, G. H., 8C2, 8C4
Jensen, K., 2A30
Joern, W., 7-35
Johnson, C. E., 2B6
Johnson, C. K., 8A35
Johnson, G. K., 2B10
Johnson, I., 2B1, 2B2, 2B3, 2B4
Johnson, James S., Jr., 8A12
Johnson, N. R., 8A3
Johnston, Harold S., 5B26
Jolley, R. L., 8D16
Jolly, William L., 5B7, 5B8, 5B9
Jones, A. R., 8A33, 8A34
Junk, G., 1A17, 1A18
Jura, George, 5B10, 5B11, 5B12, 5B13

K

Kaiser, K., 2A27
Kamin, George J., 1A1
Kaplan, L., 2A48
Kasagi, Motomu, 1A1
Katcoff, S., 3A1, 3A2
Katsanos, A., 2A2
Katz, J. J., 2A50, 2A51, 2A52
Katzin, L. I., 2A57, 2A65
Kawanishi, M., 7-11
Keller, O. L., Jr., 8A1
Kelley, M. T., 8B3
Kelly, E. J., 8A17
Kennard, S., Sr., 7-13
Kennedy, A. D., 7-2
Ketelle, B. H., 8A4, 8A8
Ketterson, J. B., 2A79
Khanna, V., 2B2
Khodai, A., 5A16
King, C. J., 5A67, 5A74, 5A75, 5A76
Kissel, George, 3B9
Klotz, Paul, 3B8
Kniseley, R. N., 1A8
Kniseley, Richard, 1A7
Koch, C. W., 5A49, 5A71
Kohn, H. W., 8A33, 8A34
Kohn, James P., 7-26
Kondo, M., 7-16

Kraus, K. A., 8A15, 8A23
Kuczynski, G. C., 7-22, 7-23, 7-24
Kuzma, L., 7-36

L

Lafferty, W. J., 6-8
Landis, D., 5A39
Larsh, A. E., 5A5
Latimer, R. M., 5A5
LaValle, D. E., 8A9
Lenz, T., 1B4
Levy, H. A., 8A24, 8A35
Lide, D. R., Jr., 6-8
Lietzke, M. H., 8A13
Lindenbaum, S., 8A14
Link, J., 5B3
Livingston, Ralph, 8A10
Lorine, D., 1B9
Ludwig, Peter K., 7-8, 7-9, 7-10, 7-11, 7-12, 7-13, 7-14
Lyon, W. S., 8B1

M

MacKenzie, D. R., 3B3
Magee, John L., 7-17, 7-18, 7-19, 7-20
Magnusson, L. B., 2A81, 2A82
Mahan, B. H., 5B14, 5B15, 5B16, 5B17
Mahlman, H. A., 8A33, 8A34
Mahony, J. D., 5A57
Maleh, I., 5A72
Malinauskas, A. P., 8C11
Malm, J. G., 2A66
Mang, H. J., 5A15
Mann, D. E., 6-5
Manning, D. L., 8B2
Manowitz, B., 3B5, 3B6
Markowitz, S. S., 5A29, 5A31, 5A57, 5A58
Marshall, W. L., 8C6, 8C7
Martin, D. S., Jr., 1A22, 1A23, 1A24
Mason, E. A., 8D3
Mason, G. W., 2A86, 2A88, 2A89
Matheson, M. S., 2A44, 2A46, 2A47
Matsumoto, C., 1A6
McBeth, R. L., 2A63
McBride, J. P., 8D13
McColm, D., 5A72, 5A73
McCusker, P. A., 7-5, 7-6, 7-7, 7-32, 7-34
McDowell, W. J., 8D1
McHarris, O., 5A72
McHarris, W., 5A10
McKinley, John D., 6-1
McLaughlin, R. D., 5A55, 5A56
McNesby, James R., 6-3
Menendez, M. G., 8A20
Meriwether, J. R., 5A33, 5A34
Mesich, F. G., 1A29
Metta, D. N., 2A7
Metzger, William H., Jr., 6-10
Meyer, B., 5B4
Meyer, R. E., 8A18
Michel, M. C., 5A22
Miller, R., 5A61
Milsted, J., 2A1, 2A7, 2A8
Minturn, R. E., 8A20
Mitchell, J. D., 7-17
Mohr, W. C., 2A33
Moon, J. S., 5A60
Moore, G. E., 8A21
Moreland, P., 2A27
Mori, M., 2A73
Moriwaki, Peter T., 7-39
Mosier, D., 5A9
Mossotti, V., 1A8
Mozumder, A., 7-18
Mrochek, J. E., 1A2
Mueller, Francis X., 7-32
Mukkergi, S., 2A9
Muller, R. H., 5B27
Mullin, C. R., 7-8
Murdoch, Lawrence, 1B6
Myers, R., 5B17

N

Nakamura, M., 5A40
Nash, J. B., 5A58
Nelson, F., 8A15
Newman, Leonard, 3B8
Newton, A. S., 5A44, 5A45, 5A59
Nichol, A., 5A55
Niemann, R. L., 2A53
Nierenberg, W. A., 5A13
Nishikawa, M., 7-5
Novakov, T., 5A3
Nowlin, Duane, 1A26
Noyes, W. A., Jr., 2A49

O

Okabe, Hideo, 6-3
Okada, M., 2A73
O'Kelley, G. D., 8A3, 8A5, 8A6
Olander, Donald R., 5B18, 5B19, 5B20, 5B21, 5B22, 5B23
O'Laughlin, J. W., 1A2
Olmsted, John, III, 5A44
Olson, W. B., 6-8
Osborne, D. W., 2A79, 2A80
Otsuki, H., 5A62
Oye, H., 2A63

P

Panontin, J. A., 2A9, 2A10, 2A11
Pape, A. J., 5A29
Parker, R., 1A2
Parker, V. B., 6-11
Parkinson, W. W., 8C1
Patterson, J. H., 2A28
Pehl, R. H., 5A27, 5A28
Peppard, D. F., 2A86, 2A88, 2A89
Perlman, I., 5A6, 5A8, 5A9, 5A10
Perlman, M., 3A1
Perlman, M. L., 3A2
Person, L. W., 2A70

Peterson, D. B., 7-2, 7-3, 7-4, 7-5, 7-6, 7-7
Philip, Jose, 7-31
Phillips, H. O., 8A23
Phillips, N. E., 5B24
Piccirelli, R., 6-7
Plasil, F., 5A16, 5A19
Porile, N., 3A1
Porter, F. T., 2A23
Poskanzer, A., 3A1
Postmus, C., Jr., 2A82
Povinelli, R., 7-13
Powell, Jack E., 1A25, 1A26, 1A27
Prados, J. W., 8D7
Pugh, H., 5A30, 5A32

Q

Quane, D., 7-35
Quarterman, L. A., 2A67
Quist, A. S., 8C6

R

Raaen, V. F., 8A28
Rabani, J., 2A44
Rainey, W. T., Jr., 8C2
Rajnak, Katheryn, 5A43
Ramsey, B. N., 1A20
Rasmussen, J. O., 5A7, 5A15, 5A17
Rauh, E. G., 2A54, 2A55
Ravindran, N., 2A14
Redlich, M. G., 5A14
Reed, G. W., Jr., 2A29
Reeder, Paul, 5A31
Reese, Robert M., 6-4
Rein, R., 7-11
Reynolds, F. L., 5A51
Rice, Francis Owen, 7-25
Riley, J. F., 8A33, 8A34
Robinson, H. P., 5A12
Robinson, L. B., 5A39
Roddy, J. W., 8D1
Rony, P., 5A66
Rosenstock, Henry M., 6-4
Rossi, Grace Francis, Sr., 7-32
Rubinson, W., 3A2
Rudolph, P. S., 8A33, 8A34
Russell, David R., 1A11
Ryon, A. D., 8D4

S

Saha, J., 7-27
San Giovanni, J., 1B1
Sauer, M. C., 2A41
Saxton, J. A., 5A63
Sayre, E. V., 3A12, 3A13
Schaeffer, O. A., 3A3
Schmidt, K., 2A46
Schmitt, Mo. F. M., 7-18
Schneggenburger, R., 7-35
Schoen, Louis J., 6-5
Scholle, W., 1B1
Schreiner, F., 2A80
Schroeter, S., 7-28
Schwartz, L. L., 2A10, 2A11
Schwarz, H. A., 3A5
Sciamanna, A. F., 5A45, 5A59
Secoy, C. H., 8C3, 8C8
Sederholm, Charles H., 5B25
Selig, H., 2A66
Seltzer, S., 3A7
Sengers, J., 6-7
Serewicz, Aubrey J., 1A11
Settle, J. L., 2B12
Shalimoff, G. V., 5A56
Sheft, I., 2A66
Sherry, E., 2A71
Shetlar, M., 5B5
Shirley, D. A., 5A1, 5A2, 5A47, 5A48
Shuck, D., 1B7
Siegel, S., 2A71
Siivola, A., 5A11
Sikkeland, T., 5A5, 5A20, 5A21
Silva, R. J., 8A2
Singh, A., 2A57
Sisson, D., 5A24
Sjoblom, R., 2A1, 2A8
Skelly, D., 7-16
Slater, L., 3B5, 3B6
Slavin, M., 3A13
Slobodrian, R. J., 5A25, 5A26
Sloth, E. N., 2A53, 2A59, 2A68
Smeggil, John, 1A21
Smentowski, F. J., 1A12, 1A14
Smith, C. F., 5A29
Smith, G., 2A72
Smutz, Morton, 1B8
Soldano, B. A., 8C8
Sortland, D., 5A69
Spedding, F. H., 1A13
Spence, D., 7-12
Srivastava, S., 7-4
Steffen, R., 2A25
Stehney, A., 2A12
Stehney, A. F., 2A13
Stein, L., 2A58, 2A64, 2A66
Steinberg, E. P., 2A9, 2A10, 2A11, 2A13
Stensland, W. A., 1A28
Stephens, F., 5A10
Stephens, F. S., 5A35, 5A36
Stevens, C., 2A27
Stevenson, F. D., 1B4, 1B9
Stewart, D. C., 2A31, 2A33
Stoenner, R. W., 3A1, 3A13
Stone, N. J., 5A1
Story, T., 5A46
Stoughton, R. W., 8A7, 8A13, 8A19
Strain, H. H., 2A32
Street, K., 5A46
Street, K., Jr., 5A44
Strickland, Gerald, 3B4
Studier, M. H., 2A53, 2A59, 2A68
Subrahmanyam, V., 5A9
Sugarman, N., 2A9
Sutin, N., 3A8
Suzuki, Y., 1A27
Svec, H. J., 1A17, 1A18
Sweeney, W., 5A68
Swiatecki, W., 5A16
Sworski, T. J., 8A33, 8A34

T

Taki, Ko, 7-1
Taub, I. A., 2A41
Taylor, E. H., 8A20, 8A21
Templeton, D. H., 5A41
Thalmayer, C., 2A83, 2B5
Thill, B., 7-28
Thoma, R. E., 8C10
Thomas, J. K., 2A42, 2A43
Thompson, H. B., 1A9
Thompson, S. G., 5A16, 5A17, 5A18, 5A19
Thoresen, R., 5A8
Thorn, R. J., 2A54, 2A55
Tobias, Charles W., 5B29, 5B30
Tomkins, F. S., 2A22, 2A72
Toogood, G., 2A58, 2A60, 2A61
Torrey, H., 1B1
Treytl, W., 5A24
Trusk, I. Ambrose, 7-38
Tsuda, S., 7-15
Tucker, R. C., 1A24
Turkevich, A., 2A28
Turkevich, A. L., 2A29

U

Unik, J. P., 2A5, 2A15, 2A17, 2A19
Urzendowski, M. Rosalie, Sr., 7-33

V

Vandegrift, A. E., 5A64
Vandenbosch, R., 2A3, 2A15
Veleckis, E., 2B4
Venkatu, D. A., 7-24
Vermeulen, T., 5A60, 5A61, 5A62, 5A63, 5A64, 5A65
Voigt, A. F., 1A28, 1A29
Vonach, H. K., 2A2, 2A3, 2A4, 2A6

W

Wadsworth, M. E., 8D14
Wagman, D. D., 6-11
Wagner, F., Jr., 2A23
Wahlgren, M. A., 2A31, 2A33, 2A34
Waki, H., 1A5
Walker, A., 2A60, 2A62
Walling, M. T., Jr., 4-1, 4-2, 4-3
Wallmann, J. C., 5A42, 5A53, 5A54
Walmsley, D. A. G., 7-3
Walsh, R., 5B3, 5B4, 5B5
Walsh, William, 1B5
Walter, Joseph L., 7-33, 7-39
Walter, K., 1B4
Walters, R. R., 2A54, 2A55
Wasan, D. T., 5A70
Weaver, Boyd, 8D1
Weber, Herman, 1A13
Weeks, J. L., 2A47
Weil, J., 2A73
Weilgoz, K., 2A9
Welna, Walton, 7-29
Weston, R. E., Jr., 3A7
Wexler, S., 2A38, 2A39
Whatley, M. E., 8D4
Whatley, W. E., 8D6
White, J. C., 8A9, 8B1, 8B2, 8B4
Wickman, H. H., 5A47, 5A48
Wilcox, N. A., 1A3
Wilke, C. R., 5A67, 5A68, 5A69, 5A70
Wilkins, B. D., 2A5
Willard, H. B., 8A4
Wilzbach, K., 2A48
Wing, J., 2A3, 2A34
Winge, R., 1A6
Winsberg, L., 2A10, 2A11, 2A13, 2A16
Winslow, G. H., 2A54, 2A55
Wodetzki, C. M., Sr., 7-5, 7-6
Wolf, A. P., 3A6
Wolfsberg, M., 3A7
Woods, W. M., 8D6
Worden, E. F., 5A56
Wright, P. M., 2A73
Wybourne, B. G., 2A61, 2A76
Wymer, R. G., 8D15

Y

Yamabe, S., 5A25, 5A26
Yosim, S. J., 7X1

Z

Zalkin, A., 5A41
Zeleznik, P. J., Sr., 7-7
Zittle, H. E., 8B4